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13. ABSTRACT

The compound $Fe(NO_3)_3.N_2O_4(NO^+Fe(NO_3)_4^-)$ was previously identified as the principal constituent of deposits responsible for flow-decay of liquid propellant N_2O_4 in steel systems. In the light of this, an extensive investigation of N_2O_4 adducts of $Fe(NO_3)_3$ has been carried out including synthesis, analysis, vibrational spectroscopy and X-ray studies. This work indicates that the constituent species of the solid adducts $Fe(NO_3)_3xN_2O_4$ (where x is typically 1.0-1.5) are NO^+, NO^+(solvated by NO_2 or N_2O_4), $Fe(NO_3)_4^-$ and N_2O_4. The behavior of these adducts has also been studied in HNO_3 solution and in HNO_3/N_2O_4 mixtures, since the presence of HNO_3 in propellant N_2O_4 was suspected to influence the physical and chemical nature of the flow-decay deposit and may be partially or perhaps primarily responsible for corrosion of steel. The properties of the $Fe(NO_3)_3xN_2O_4/HNO_3/N_2O_4$ system are interpreted in terms of a gross modification of the HNO_3/N_2O_4 phase diagram by $Fe(NO_3)_3xN_2O_4$. A flow apparatus has been constructed so that flow-decay deposit may be collected and its chemical identity and physical form studied as a function of the "water" (HNO_3) content of N_2O_4 (monitored by ^1H n.m.r.). A number of projected investigations is also discussed. These include studies of dissociation vapor pressures of $Fe(NO_3)_3xN_2O_4$ to elucidate the stoichiometry of stable adducts and scanning electron microscopy before and after exposure to dilute solutions of NOCl in liquid N_2O_4 for known lengths of time. Assessment of the importance of NOCl as a primary corrosive agent should then be possible. Similar experiments could be carried out with solutions of HNO_3 in N_2O_4.

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A flow apparatus has been constructed so that flow-decay deposit may be collected and its chemical identity and physical form studied as a function of the "water" (HNO_3) content of N_2O_4 (monitored by ^1H n.m.r.). A number of projected investigations is also discussed. These include studies of dissociation vapour pressures of $Fe(NO_3)_3xN_2O_4$ to elucidate the stoichiometry of stable adducts and scanning electron microscopy before and after exposure to dilute solutions of NOCl in liquid N_2O_4 for known lengths of time. Assessment of the importance of NOCl as a primary corrosive agent should then be possible. Similar experiments could be carried out with solutions of HNO_3 in N_2O_4.

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1. INTRODUCTION

In use as an oxidiser component of bipropellant rockets, liquid dinitrogen tetroxide, which has been stored in iron or steel containers, flows through narrow orifices or fine mesh filters. The flow rate may sometimes decay as a result of clogging at such locations by a "flow-decay deposit", and this report describes work carried out at the University of Nottingham during the period July 1970 to July 1971 on the nature of this deposit. There appears to be, as yet, no firm agreement as to the physical nature of this deposit. Thus, earlier reports describe this material as either solid[1] or gelatinous[2] in nature. However, it seems to be generally agreed that the compound $Fe(NO_3)_3.N_2O_4$ $(NO^+Fe(NO_3)_4^-)$ is the principal constituent of such deposits. This compound was first isolated in these laboratories,[3,4] and in previous work we had demonstrated that the compound is a solid in the presence of pure, dry liquid N_2O_4. Nevertheless, many aspects of the chemistry of the compound remain to be examined and this necessarily forms the major theme of our work. One major aspect concerns the formation of gels. We have felt that this is unlikely to arise from the agency of N_2O_4 alone, and must therefore be attributed to one (or more) of the impurities present in propellant N_2O_4. In the present studies, it was considered that the impurity most likely to convert $Fe(NO_3)_3.N_2O_4$ into a gel is HNO_3, arising from the so-called "water" content (ca 0.1%) of the N_2O_4. Indeed, it was suspected that the physical nature of the flow-decay material may well be a function of the "water"

content. In an attempt to resolve the question of the physical form of the flow-decay deposit, its precise composition and the influence of "H_2O content" of the N_2O_4 upon its identity, a flow apparatus has been constructed which is designed to permit facile collection and identification of the deposit. ^1H n.m.r. has been used to determine the "H_2O content" of the N_2O_4 employed in flow experiments and the observations to date are described in Section 3.

To eliminate the flow-decay problem, the formation of flow-decay compound must be prevented, or its properties suitably modified so that it is retained in solution in the propellant N_2O_4. Both approaches demand the fullest possible knowledge of the synthesis, constitution and properties of adducts between N_2O_4 and $Fe(NO_3)_3$. In the course of these studies it became clear that although the compound $Fe(NO_3)_3.N_2O_4$ can be prepared, materials whose composition may be written $Fe(NO_3)_3xN_2O_4$, $x > 1$ are the initial products of attempts to prepare $Fe(NO_3)_3.N_2O_4$, and are only with difficulty brought to the 1:1 composition. The nature of these materials clearly is of great relevance to the technological problems of handling N_2O_4 in steel containers. The constitution of these adducts, and in particular the bonding of the "additional" N_2O_4 was therefore considered of great importance, and the work to date in this field is described in Section 2. In view of the suspected influence of HNO_3 on the nature of the flow-decay deposit, extensive laboratory investigations of $Fe(NO_3)_3xN_2O_4$ in HNO_3 solution

and in HNO_3/N_2O_4 mixtures have been carried out and are reported in Sections 4 and 5.

This is an annual report which is written half-way through a two-year investigation. The main purpose of the report is therefore to describe the experiments which have been carried out, with an indication, where appropriate, of the ways in which we hope to develop these experiments. We have reduced "conclusions" to a minimum at this stage of the work, since they will be more appropriate in the Final Report. In Section 6, however, we have outlined some new avenues of investigation which we hope to explore during the second year of the Agreement.

In concluding this introduction it must be emphasised that great care has been taken to exclude moist air throughout all the experimental work described in this report.

2. THE NATURE OF THE ADDUCTS BETWEEN $Fe(NO_3)_3$ AND N_2O_4

During the course of the work described in this report, the known methods for the preparation of N_2O_4 adducts of $Fe(NO_3)_3$ have been reinvestigated and, where possible, refined. Additionally, certain new procedures have been developed.

(i) Methods of preparation

a) The reaction of $Fe(CO)_5$ and N_2O_4 in CCl_4

A solution of $Fe(CO)_5$ in CCl_4 was slowly added to excess N_2O_4 in CCl_4, with stirring, at 0^oC. The experimental arrangement ensured that mixing of the reactants took place under the surface of the N_2O_4 solution in order to minimise the formation of the product $FeO(NO_3)$[5] by vapour phase reaction. A vigorous reaction occurred and a mixture of two products was formed, a yellow smoke (presumed to be $FeO(NO_3)$) and a gummy solid. This mixed product was isolated on a filter-stick, evacuated briefly to remove solvent and excess reactants and was then left to stand for 24 hours in contact with fresh dry N_2O_4, which effects complete conversion of $FeO(NO_3)$ to an N_2O_4 adduct of $Fe(NO_3)_3$.[5] The product was filtered and dried by evacuation.

b) The reaction of $FeCl_3$ and N_2O_4 in EtOAc

This was the first discovered synthetic route to the compound $Fe(NO_3)_3.N_2O_4$[3] and was considered to be the method of choice at the commencement of the present work. (As substantial quantities of the compound $Fe(NO_3)_3.N_2O_4$ were to be used in the laboratory experiments described in Sections 4 and 5 of this report this preparation was performed on a relatively large scale).

A.R.$FeCl_3$ (50 g) was dissolved in dry EtOAc (200 ml) and the solution was added to dry N_2O_4 (200 ml). The mixture was set aside overnight. Excess N_2O_4 and most of the EtOAc was then removed by evacuation (10^{-2}mm) yielding a dark red viscous syrup. Addition of a large excess of dry N_2O_4 resulted in immediate precipitation of yellow/brown crystals. These were isolated using a filter-stick and washed with dry N_2O_4. Addition of dry N_2O_4 to the filtrate yielded a further crop of crystals. In some preparations using this method, the product was found to contain a small amount of Fe_2O_3 (identified by I.R. spectroscopy). This contaminant was removed by dissolution of the product in either EtOAc or $MeNO_2$ followed by reprecipitation and washing with N_2O_4.

c) The reaction of $FeCl_3.NOCl$ and N_2O_4

Metallic iron does not react at room temperature with liquid N_2O_4 or mixtures with EtOAc but the addition of small quantities of $FeCl_2$ or $FeCl_3$ to an EtOAc solution promotes a steady reaction with the metal.[4] This behaviour results from the production of NOCl by solvolysis of the added chloride. NOCl reacts vigorously with metallic iron[6,7] to give $FeCl_3.NOCl$ which in excess N_2O_4 is expected to undergo complete solvolysis to give the corresponding compound in the N_2O_4 system:

$$\text{i.e. } FeCl_3.NOCl + 4N_2O_4 \rightleftharpoons Fe(NO_3)_3.N_2O_4 + 4NOCl.$$

The advantage of this reaction is that it should provide a direct route to the desired N_2O_4 adduct without the addition (and the need for subsequent removal) of an organic donor solvent.

NOCl was condensed on to spectroscopically pure iron at

$-78^{o}C$ and allowed to warm slowly to room temperature. A steady reaction occurred and a yellow-brown powder was deposited. This was evacuated (10^{-2}mm) overnight to remove excess NOCl, and a large excess of N_2O_4 was then added. A gentle reaction occurred over about three days. Excess N_2O_4 was then removed by evacuation (10^{-2}mm) and the resulting powder tested for chloride. If necessary, the powder was treated with further amounts of N_2O_4 until the chloride test was negative.

A modification of this experiment which is currently under investigation involves reaction of iron with N_2O_4 containing a small proportion of NOCl which should function as a catalyst. Thus the initial product should be $FeCl_3.NOCl$ from which NOCl will be regenerated by the above solvolytic reaction. The reaction should continue until all the iron has reacted, provided NOCl is retained in solution. This modification will allow reaction with metallic iron to be completed in a single stage and should facilitate the complete elimination of chloride without the necessity for repeated treatment with N_2O_4.

d) Attainment of the composition $Fe(NO_3)_3.N_2O_4$

As stated in the Introduction, the initial product arising from each of the above preparative methods usually contains an amount of N_2O_4 in excess of that required by the formulation $Fe(NO_3)_3.N_2O_4$ ($NO^+Fe(NO_3)_4^-$) and exhibits bands due to molecular N_2O_4 in the infra-red spectrum (see Section 2(iii) a)). The actual N_2O_4 content of individual products was monitored by use of the analytical techniques described in Section 2(ii).

The precise composition $Fe(NO_3)_3.N_2O_4$ may be achieved where necessary by evacuation (10^{-2}mm at about $20^{o}C$) of the initial

products of the above reactions for several days during which time the molecular N_2O_4 content of the compound may be monitored by intermittent nitrite analysis (Section 2(ii) b)) and infra-red spectroscopy (Section 2(iii) a)). The reluctance with which this iron compound loses the N_2O_4 which is in excess of the above formulation is one of its most striking features and one which is not encountered to any comparable extent in N_2O_4 adducts of other metal nitrates.

(ii) Analysis

The following procedures were adopted in the analysis of the products obtained by the methods of Section 2(i).

a) Total nitrogen by the Kjeldahl method

Total nitrogen content was determined by a modified Kjeldahl method using Devarda's Alloy. Adducts were first hydrolysed in alkali to ensure retention of all nitrogen in the form of NO_3^- and NO_2^-. Hydrolysates were prepared by a "closed-bottle" technique in which a known weight of sample was placed in a thin-walled glass bulb which was broken in a sealed vessel, in the presence of a known volume of 2M sodium hydroxide. Aliquots of this solution were then treated with Devarda's Alloy and further sodium hydroxide in a Kjeldahl apparatus and the liberated NH_3 was steam distilled into a known volume of standard boric acid which was titrated against standard HCl using a mixture of bromocresol green and methyl red as indicator.

b) N_2O_4 content by Ce(IV) titration of NO_2^-

Further aliquots of the above hydrolysate were used. Each aliquot was added to a known excess of acidified standard ceric sulphate solution which was back-titrated against standard ferrous ammonium sulphate solution. N_2O_4 (or NO^+)

yields an equimolar amount of NO_2^- on alkaline hydrolysis.

c) Iron by atomic absorption

Iron determinations were carried out by means of a Southern Analytical A3000 Atomic Absorption Spectrometer. Solutions of adducts were prepared in dilute nitric acid and diluted appropriately. A calibration curve was obtained using solutions of known iron concentration. These were prepared by dissolution of spectroscopically pure iron in dilute nitric acid to give a nominally 100 ppm stock solution which was then diluted with dilute nitric acid to obtain standards in the concentration range required for optimum sensitivity.

(iii) Vibrational Spectroscopy

a) Infra-red spectra

Infra-red spectra of the solid adducts were recorded on a Perkin-Elmer 457 spectrometer using AgCl cell windows. Nujol mulls were prepared in a dry box. Infra-red spectroscopy was used to follow the removal of molecular N_2O_4 in excess of that required by the formulation $Fe(NO_3)_3.N_2O_4$. The presence of molecular N_2O_4 is recognised by the appearance of bands at 1740, 1251 and 742 cm^{-1}.[8]

A typical spectrum of the compound $Fe(NO_3)_3.N_2O_4$ is shown in Fig. 2.1 and the bands are listed and assigned in Table 2.1. This spectrum provides evidence for formulation as $NO^+[Fe(NO_3)_4]^-$ since it is virtually identical in the covalent nitrate region to that of the compound $(Ph_4As)^+[Fe(NO_3)_4]^-$ which was shown to contain a discrete anion of dodecahedral (D_{2d}) symmetry by means of a single crystal X-ray investigation recently completed in these laboratories.[9] Four symmetrically bidentate nitrate groups are disposed around iron(III) in this anion. No evidence for the presence of NO_3^- ion or nitrato-

Table 2.1.

Vibrational Spectrum of $Fe(NO_3)_3.N_2O_4$

Infra-red (cm^{-1}) Nujol mull	Raman (cm^{-1})	Assignment
2298 w	2302 s	NO^+ stretch
2230 w,b		NO^+ stretch
1598 s	1608 s	ν_1 N-O stretch
1548 vs,b	1570 s	ν_1 N-O stretch
1295 s,b	1263 mw	ν_4 NO_2 asymm. stretch
1018 s,s	1030 m	ν_2 NO_2 symm. stretch
798 s,s	784 m	ν_6 out of plane bend
764 vs,s	769 m	ν_3 NO_2 asymm. bend
	364 m	metal-oxygen stretch

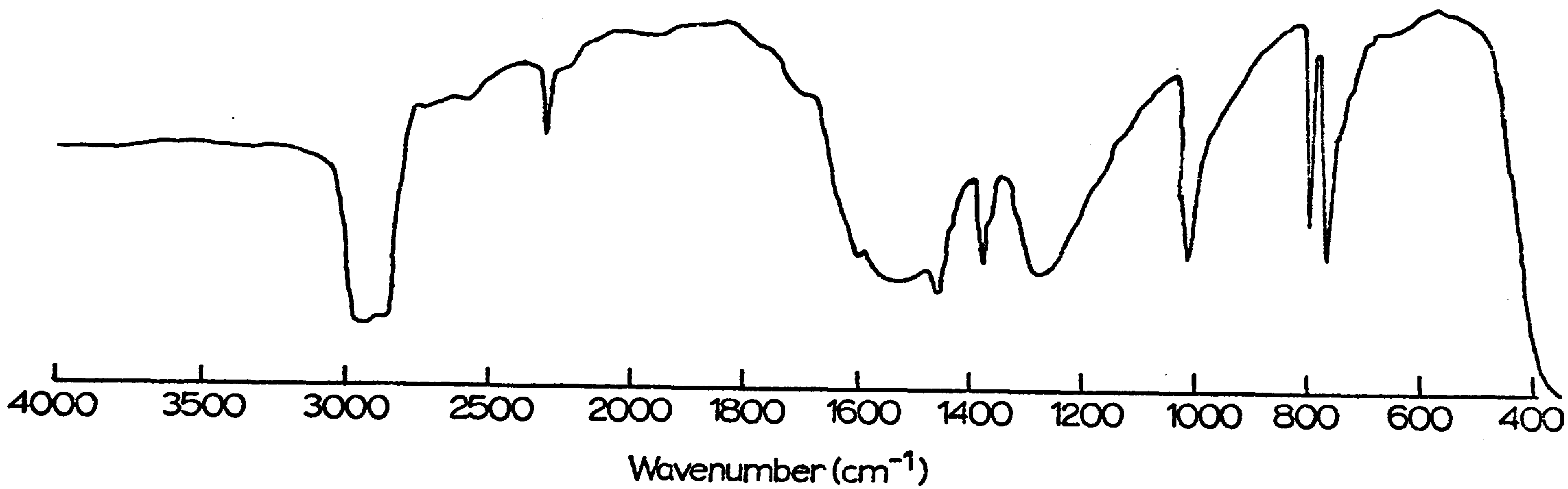


Figure 2.1 **I.R. Spectrum of $Fe(NO_3)_3 \cdot N_2O_4$**

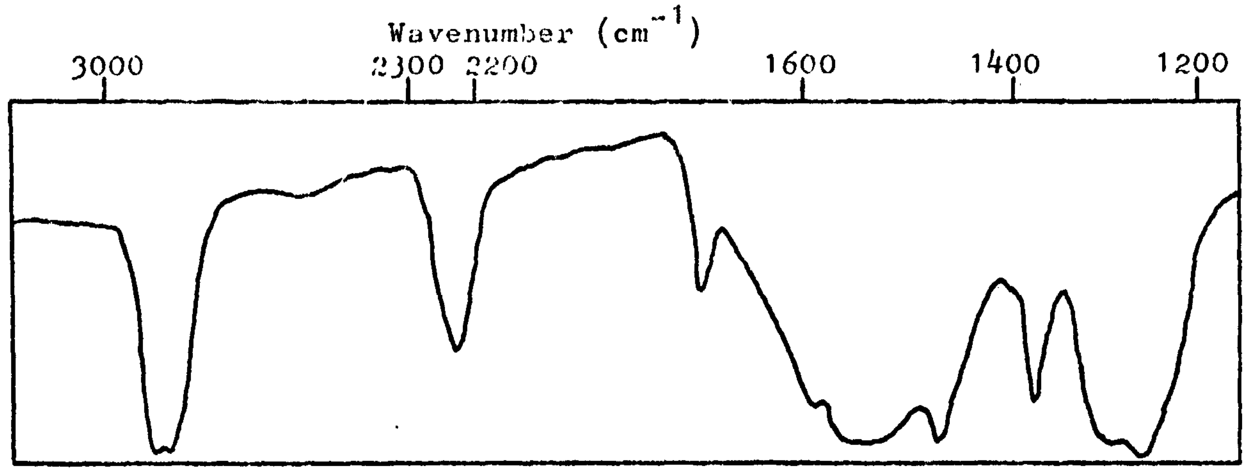
species other than $Fe(NO_3)_4^-$ is obtained from the infra-red spectrum of $Fe(NO_3)_3.N_2O_4$. The bands attributable to the presence of this anion $Fe(NO_3)_4^-$ in $Fe(NO_3)_3.N_2O_4$ are thus assigned in Table 2.1 in terms of bidentate bonding of nitrate groups and are uninfluenced by the mode of preparation of the compound or by the presence of N_2O_4 in excess of this formulation.

The infra-red spectrum of the initial (unevacuated) products of the preparative reactions described in Section 2(i) showed a very intense band at 2230 cm^{-1} (Fig. 2.2(a)), together with the expected bands due to molecular N_2O_4.[8] On evacuation of the compound (10^{-2}mm) for 3 days the molecular N_2O_4 bands and the band at 2230 cm^{-1} decreased in intensity and a further band appeared at 2298 cm^{-1} (Fig. 2.2(b)). After evacuation for a further 3 days the two bands in the NO^+ region were of comparable intensity (Fig. 2.2(c)) and after 2 weeks the 2298 band was the more intense with the 2230 band as a shoulder (Fig. 2.2(d)). On dissolving the evacuated compound in ethyl acetate and reprecipitating with N_2O_4 the spectrum reverted to that of Fig. 2.2(a). These observations lead to the conclusion that excess N_2O_4 may be associated in some way with the NO^+ cation in an analogous manner to that known for diethylnitrosamine[10,11] in which two molecules of this solvent coordinate to NO^+, producing a consequent shift in the infra-red absorption band.

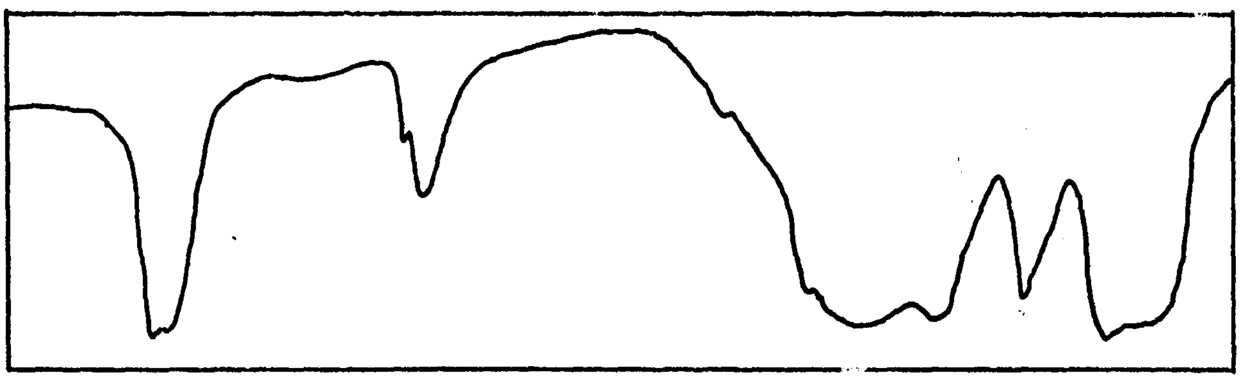
This leads to the prediction that the compound $[(N_2O_4)_2NO]^+Fe(NO_3)_4^-$ ($Fe(NO_3)_3.2N_2O_4$) may be a recognisable entity. Alternatively NO^+ may associate with NO_2 to form the species $(NO_2)NO^+$ which Goulden and Millen[12,13] suggested as being present in solutions of N_2O_4 in 100% HNO_3 on the basis

Figure 2.2

Change in I.R. spectrum on altering the composition of $Fe(NO_3)_3xN_2O_4$

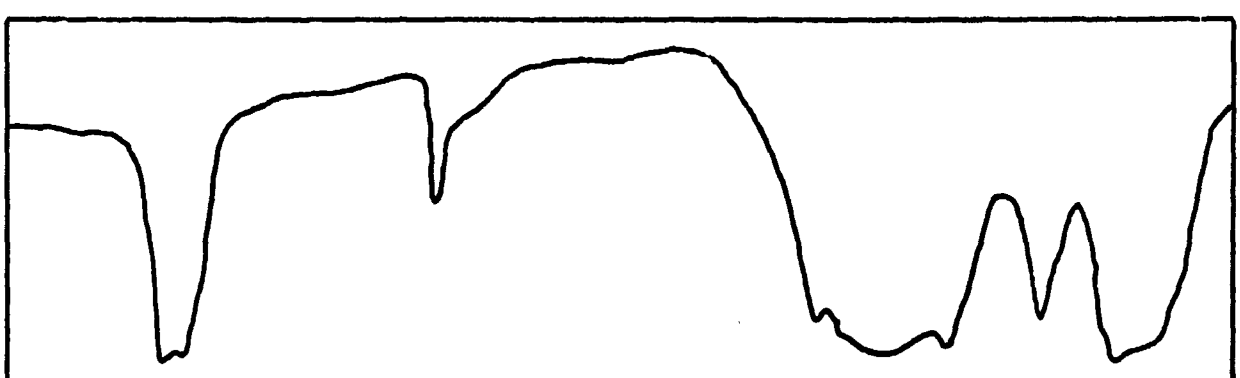


(a) Sample of $Fe(NO_3)_3xN_2O_4$ as prepared from $NOFeCl_4$.



(b) Sample as above after 3 days evacuation (10^{-2}mm).

(c) Same sample after 6 days evacuation (10^{-2}mm).



(d) Same sample after 2 weeks evacuation (10^{-2}mm).

of a Raman spectroscopic study. Thus, the species $[(NO_2)NO]^+Fe(NO_3)_4^-$ may also be an identifiable entity. Whatever the nature of the association causing the change in NO^+ band position, the net result is the same i.e. a lowering of the $N-O^+$ bond order and thus a lowering of the energy of vibration.

It is also relevant to note that association of NOCl and NO^+ is considered to occur in certain metal halide-nitrosyl chloride adducts.[14] Thus it is apparent that the NO^+ ion displays a willingness to enter into associations of this type.

b) Raman spectra

The Raman spectrum of $Fe(NO_3)_3.N_2O_4$ was recorded using a Spectra-Physics 125 He-Ne laser as an excitation source (output approx. 60mW at 632.8 nm). The sample was contained in a sealed glass cell. The observed bands are listed and assigned in Table 2.1. Further support for the bidentate nitrate assignments given in this Table is obtained from the sequence of relative intensities of the three highest-frequency Raman shifts attributable to nitrate fundamentals at ca 1600, 1250, and 1000 cm^{-1}, i.e. the sequence:- strong, weak, strong. This agrees with the general observation that for symmetrically bidentate species the band at ca 1250 cm^{-1} (the N-O antisymmetric stretch) is weak and without exception the least intense of the three bands. In the case of unidentate nitrato-complexes, however, this band is generally fairly strong and is by no means the least intense of the three bands.[15] The alternative method of distinguishing uni- and bidentate bonding in nitrato-complexes by means of depolarisation ratios is not applicable to solids, but is described for solutions in HNO_3 in Section 4(iii).

(iv) Formulation of the adducts between $Fe(NO_3)_3$ and N_2O_4 as $Fe(NO_3)_3xN_2O_4$

The vibrational spectrum of material analytically $Fe(NO_3)_3.N_2O_4$ has shown it to be $NO^+Fe(NO_3)_4^-$. However, the initial product from each of the preparative routes described in Section 2(i) had a higher N_2O_4 content than that for $Fe(NO_3)_3.N_2O_4$, and these products were for convenience written as $Fe(NO_3)_3xN_2O_4$. However, the vibrational spectroscopy of these materials indicates that they contain $Fe(NO_3)_4^-$, NO^+ and/or a 'modified' NO^+ band (depending on the N_2O_4 content) and (usually, but not always) molecular N_2O_4. The maximum value so far observed for x in the formulation $Fe(NO_3)_3xN_2O_4$ is <u>ca</u> 2.5, in a product from the direct reaction between $Fe_3(CO)_{12}$ and N_2O_4. It would seem that the best representative formulation at this time is:

$$[NO^+, NO^+(\text{solvated})]\ Fe(NO_3)_4^- \ .\ N_2O_4$$

However, for brevity the designation $Fe(NO_3)_3xN_2O_4$ will throughout this report refer to materials of this nature, and $Fe(NO_3)_3.N_2O_4$ will be used only for materials analytically close to the 1:1 stoichiometry.

(v) X-ray powder photography

X-ray powder photographs were taken as a matter of course for all samples produced in preparative and in "extraction" experiments, described in Section 5(iv), wherever this was possible i.e. when the material was neither too wet with N_2O_4 nor gel-like. The reasons for taking powder photographs of products from the preparative experiments were two-fold. Firstly, to establish a characteristic X-ray powder photograph of $Fe(NO_3)_3.N_2O_4$ and secondly to observe any correlation between the change in the X-ray powder pattern and a change in x in the

molecular formula $Fe(NO_3)_3xN_2O_4$.

The first objective was achieved (see Table 2.2) but no significant results were obtained for the second and a further careful and detailed study to this end will be performed in the near future as follows. An X-ray photograph of powder in contact with liquid N_2O_4 will be run followed by a series of photographs of samples obtained after evacuation for increasing lengths of time.

The powder patterns were obtained using a Phillips X-ray powder diffractometer with an 11 cm camera and CuKα radiation. After measurement of films the data was fed into the computer along with the programme:- "d-spacing etc. from powder photographs", J.M. Spink, National Physical Laboratory, 1965, which has been modified by A.J. Hooper and D.J. Wood in this Department, for a KDF9 computer. Typical d-spacings and intensities are recorded in Table 2.2 (a-d).

These results are in agreement with an earlier report[1] that the compound $Fe(NO_3)_3.N_2O_4$ exists in at least two crystalline forms. One pattern is obtained repeatedly from the preparations using EtOAc, $FeCl_3$ and N_2O_4 (Table 2.2(a)) but a quite different photograph is obtained from the product of the $FeCl_3.NOCl/N_2O_4$ reaction (Table 2.2(d)). The results obtained for the $FeCl_3/EtOAc/N_2O_4$ product agree with those of earlier workers[1] for the same reaction. Also, the pattern observed for the $FeCl_3.NOCl/N_2O_4$ reaction product is identical to that of the compound prepared from $Fe(CO)_5$ and N_2O_4 and recrystallised from N_2O_4 by Soxhlet extraction.[1]

A further important point arises from the present results. The powder pattern of a product obtained by treatment of $Fe(NO_3)_3.N_2O_4$ in HNO_3 with dry N_2O_4 (see Table 2.2(c) and

Table 2.2.

X-Ray Diffraction Powder Patterns of Adducts Between $Fe(NO_3)_3$ and N_2O_4

(a) $Fe(NO_3)_3.N_2O_4$ from $FeCl_3$/EtOAc/N_2O_4 preparation

d-spacing (Å)	Intensity
6.3	100
6.0	5
5.7	80
5.2	50
4.9	20
4.7	20
4.44	20
4.23	30
3.98	2
3.66	70
3.43	60
3.20	30
3.11	40
3.06	50
2.98	60
2.91	2
2.44	30
2.35	20

(b) $Fe(NO_3)_3.N_2O_4$ from $FeCl_3$/EtOAc/N_2O_4 preparation, recrystallised from $MeNO_2$

d-spacing (Å)	Intensity
6.3	100
5.8	30
5.6	80
5.3	10
5.1	70
4.9	5
4.6	5
4.1	20
3.93	2
3.65	70
3.41	50
3.19	40
3.06	50
2.96	70
2.90	2
2.43	20
2.31	5
2.25	60
2.12	5
2.08	5
2.04	5
1.98	5
1.93	5

Table 2.2 (cont'd.)

(c) $Fe(NO_3)_3.N_2O_4$ from $FeCl_3$/EtOAc/N_2O_4 preparation, recrystallised from HNO_3/N_2O_4

d-spacing (Å)	Intensity
6.3	100
5.7	70
5.1	60
4.8	5
4.6	30
4.42	2
4.21	5
3.61	50
3.41	50
3.21	30
3.08	40
2.98	50
2.61	5
2.43	30
2.27	30

(d) $Fe(NO_3)_3.N_2O_4$ from $FeCl_3.NOCl$/N_2O_4 preparation

d-spacing (Å)	Intensity
7.3	80
7.0	80
6.2	90
5.6	20
5.05	2
4.56	100
4.36	2
4.03	5
3.74	40
3.55	30
3.38	50
3.22	50
3.01	2
2.80	20
2.66	2
2.57	20
2.42	30
2.28	10
2.18	30

Sections 5(iv) a) and 5(v)) i.e. a sample recrystallised from HNO_3/N_2O_4 mixtures, is identical with that of $Fe(NO_3)_3.N_2O_4$ prepared by the $FeCl_3$/EtOAc/N_2O_4 method. Also, $Fe(NO_3)_3.N_2O_4$ recrystallised from nitromethane has a powder pattern identical with that prepared from $FeCl_3$/EtOAc/N_2O_4 (Table 2.2(b)).

(vi) Single crystal X-ray investigation (Dr. E. Nunn)

Crystals suitable for the X-ray investigation were grown from EtOAc/N_2O_4 mixtures. These were filtered and washed with dry N_2O_4 and were then loaded, still wet with N_2O_4, into 0.3 mm X-ray tubes into which a small amount of dry N_2O_4 had been distilled. This excess N_2O_4 was necessary for the maintenance of the crystalline form during the time that the tube was in the camera. The tubes were then sealed.

Data has been collected on a crystal of $Fe(NO_3)_3xN_2O_4$ using the Hilger Linear Diffractometer. The crystal is monoclinic and belongs to the space group $P2_1/c$. The unit cell dimensions are a = 10.218, b = 19.873, c = 14.337Å, β = 123°18'. A total of 1800 reflections have been recorded about the a- axis for values of h from 0 to 11. The cell dimensions and the estimated density indicate that there are probably two molecules in the asymmetric unit.

An earlier batch of crystals showed triclinic symmetry but the crystals were unsuitable for further data collection.

3. THE FLOW APPARATUS AND EXPERIMENTS

(i) Construction

One of the aims of this research is to investigate the nature of material causing flow-decay through small orifices. It was decided that the problem should be examined by two approaches:

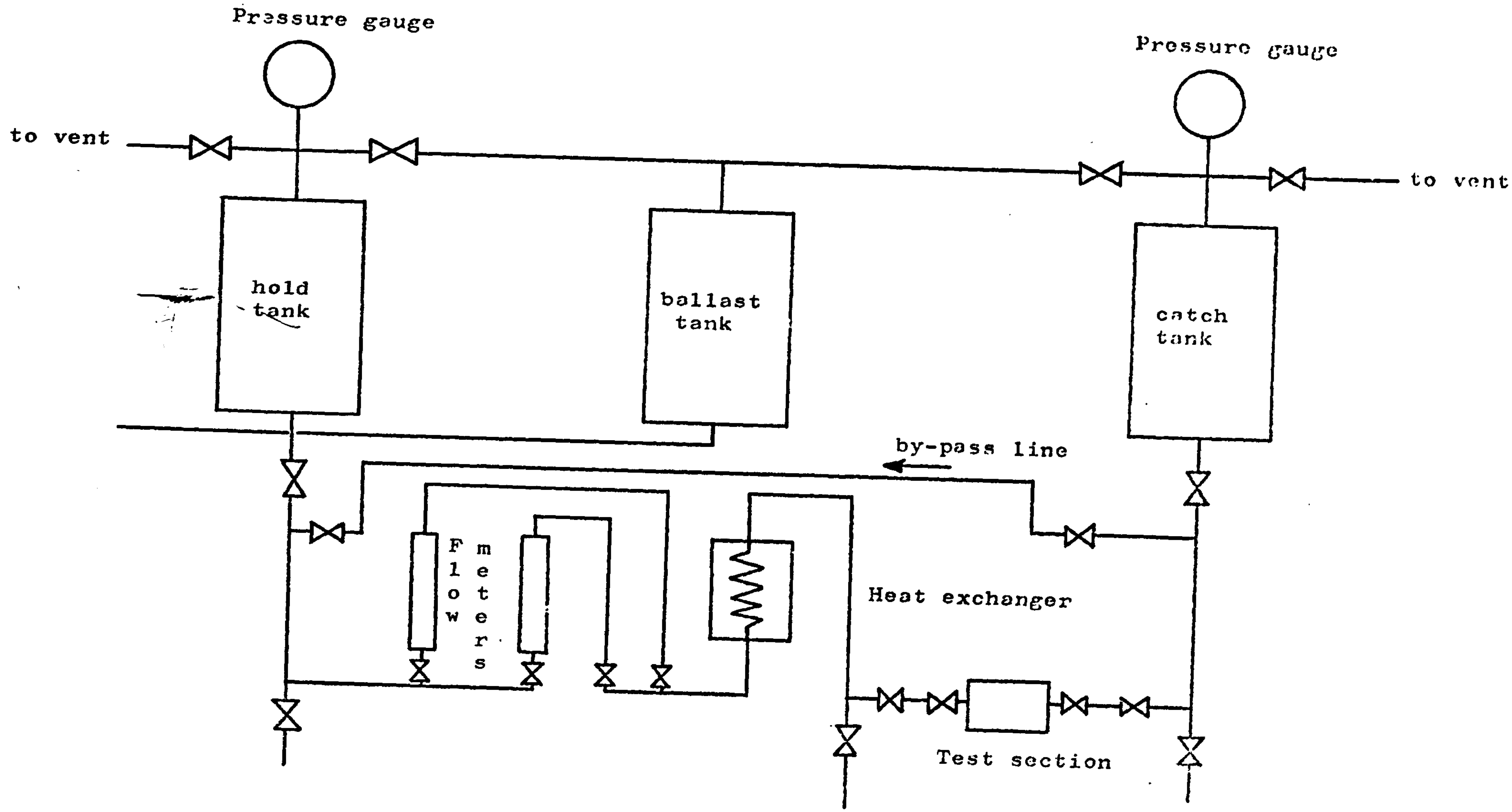
a) The construction of a flow-decay apparatus, by means of which we hoped to isolate flow-decay deposit.

b) The study of $Fe(NO_3)_3xN_2O_4$ in HNO_3 and HNO_3/N_2O_4 mixtures.

The former approach is described here, and discussion of the latter is deferred until Sections 4 and 5.

Design of the flow apparatus was based upon a system which has been used by previous workers[2] to demonstrate flow-decay. A schematic diagram of the flow apparatus is presented in Fig. 3.1. Having decided upon the design of the flow apparatus it was necessary to choose suitable materials for its construction. Glass and fluorinated plastics were unsuitable for fabrication of tanks and pipework because of fragility and constructional difficulties. Also, if the apparatus was built in glass or plastic, it would be necessary to saturate N_2O_4 used for flow runs with iron in order to induce flow-decay. It was thought at this time that inclusion of metals other than iron in the system should be avoided, and to this end mild steel was used in preference to stainless steel in the construction. Since our workshop staff had considerable experience in the machining of Teflon cone valves for use in fluorine systems, valves of this type were adapted for incorporation into the apparatus.

Figure 3.1 Schematic diagram of the flow apparatus



The quantity of glass in the system was reduced to a minimum and was eventually used only in the construction of the hold tank level indicator and in the flowmeters. This glass had been tested to pressures far in excess of those to be used in flow experiments.

Pressurisation of the system was effected by means of a cylinder of high purity nitrogen. The gas was passed through a Negretti and Zambra pressure regulating valve into a 5 gallon ballast tank. N_2O_4 was held in a 5 gallon hold tank and was passed under pressure through one of two flowmeters (depending upon the flow-rate required) and through the heat exchanger, which comprised a 20ft mild steel coil inside a cooling jacket supplied with coolant from an Ultra-Kryomat TK30D circulating refrigerant unit. From here, the cooled liquid N_2O_4 was passed through a test section (see Section 3(ii)) and into a catch tank. Both the hold and catch tanks were fitted with relief valves so that a constant predetermined pressure could be maintained during flow experiments. Each tank was also fitted with a pressure gauge. A by-pass line was constructed between the two tanks, allowing N_2O_4 to be passed directly from tank to tank i.e. circumventing the test section, heat exchanger and flowmeters if necessary.

A cylinder of N_2O_4 was connected to the apparatus by means of steel tubing and the hold tank was filled using the internal cylinder pressure to force the liquid into the system. Several of the Teflon valves showed signs of leakage, necessitating tightening of pipe connections and valve stems and upon manipulation, most of the remaining valves showed seepage of N_2O_4. The valves immediately on each side of the test section

leaked persistently and defied all efforts to arrest this by tightening. These valves were therefore replaced by steel valves. During the time used for commissioning the apparatus, most of the Teflon valves gave further trouble and a decision was made to replace these by steel ball valves with Teflon seats. It has subsequently been discovered that other workers[16] have found Teflon to be porous to N_2O_4, however, since installation of the steel ball valves no further trouble has been experienced.

Some temporary inconvenience was also encountered because a few galvanised joints and unions had inadvertently been fitted. It is well known that N_2O_4 readily dissolves zinc and the product is the adduct $Zn(NO_3)_2.2N_2O_4$ which was precipitated in the pipes. The pressuring system has been modified to give more precise control, and the apparatus was tested for leakage up to the maximum working pressure (60 psi).

(ii) Test sections and flow experiments

a) Gauze filters

Previous workers[2] observed viscous gel formation on this type of test section and an attempt has been made to reproduce this phenomenon. The test section comprised a thimble of stainless steel gauze (100 or 400 mesh or 10μ) contained in a thick glass envelope. The end flanges of steel were connected through a gasket of rubber with a Teflon insert so placed that the rubber portion made no contact with N_2O_4. Flow runs using various pressure and temperature differentials and flow-rates were performed using a 100 mesh gauze but at no time was any flow-decay material observed in the test section. The test section was illuminated using both transmitted and

reflected light and the gauze was observed using a microscope. Trouble was experienced with the Teflon gasket material, since it was apparently porous towards N_2O_4 and allowed attack of the rubber portion and subsequent major leakage. It was then decided to change to needle valve test sections in further attempts to induce flow decay, but it should be emphasised that the approach using gauze filters has not been discarded and may be re-examined at a later date using finer mesh gauzes.

b) Needle valves

The use of needle valves was prompted by the observation of a brown solid deposit on a needle control-valve adjacent to the previous gauze test section. The quantity of this material was too small to allow any characterisation but it was thought likely that more of this solid might be accumulated by using a needle valve test section. While a suitable steel needle valve was being modified for use as a test section, a Teflon-in-glass stopcock was temporarily fitted and some experiments were performed with this. Again, using the full range of variables, no flow-decay material was observed in the test section; perhaps a not too surprising result since adherence to a Teflon surface is probably difficult.

A stainless steel needle valve was fitted with glass windows so that the needle could be viewed directly, using a microscope. Under the conditions available, no accumulation of flow-decay material on the needle was observed and it became apparent that some modification of the apparatus would be necessary to induce flow-decay. The N_2O_4 in the flow

apparatus was found by ^1H n.m.r. (see Section 3(iii) below) to contain 0.12% "water" which compared closely to the usual specification of propellant N_2O_4 and should be sufficient to bring about flow-decay if the presence of HNO_3 in the system is, in fact, the cause. It is possible however that the species responsible for attack on steel vessels may be NOCl (see Section 6(ii) a)) present as an impurity in propellant specification N_2O_4. The N_2O_4 used in the above experiments was stated by the manufacturers to be chloride free and qualitative tests confirmed this. Previous workers observed that if the hold tank was "conditioned" with N_2O_4 by warming to ca 35^oC, flow-decay could be induced with relative ease. The flow apparatus is at present being modified to include heating and temperature recording equipment and further discussion of this is deferred until Section 6(iii).

(iii) Determination of "water" content of liquid N_2O_4 by ^1H n.m.r.

At the commencement of the present research programme, the necessity for a rapid and convenient method of determining the "water" content of samples of liquid N_2O_4 used in the flow apparatus and in other laboratory investigations was immediately recognised. The use of proton n.m.r. for this purpose has been reported previously.[17,18] Initial experiments in these laboratories were conducted using a Varian HA 100 (100 MHz) n.m.r. spectrometer, on account of its higher sensitivity than the 60 MHz Perkin-Elmer R.10 spectrometer, also available in this Department. However it is necessary with the 100 MHz instrument to incorporate with the sample a standard proton containing material to provide a suitable locking signal. Benzene and chloroform were tried

as internal standards (i.e. dissolved in the N_2O_4) and tetra-methyl silane as an external standard (i.e. not dissolved in the N_2O_4, but placed in the sample tube in a small glass capillary). However, none of these was entirely satisfactory, benzene because of nitration (and hence increase of the proton content of the N_2O_4) in samples with high water content; chloroform because of the proximity of the "water" and chloroform resonances, which produced attendant difficulties in locking and integration of signals, and tetra methyl silane because of the diminution of the sample volume (and hence "water" signal) by displacement on insertion of the glass capillary. For these reasons, subsequent estimations were carried out on the Perkin-Elmer R.10 (60 MHz) spectrometer, which operates in a non-locked mode, and hence needs no reference standard.

A series of calibration standards was prepared from small weighed amounts of water (5 figure balance) and weighed amounts of dry (i.e. distilled from phosphoric oxide) N_2O_4. N.m.r. samples in 0.7 mm wall-thickness soda glass tubes were frozen in liquid N_2, evacuated and sealed. These tubes were found to be quite safe under the conditions used; each sealed sample was heated to 40°C before estimation (n.m.r. probe temperature 31°C), but no tube exploded. Within experimental error a linear calibration graph of signal integral against %"water" content was obtained. N_2O_4 distilled from phosphoric oxide was shown in this manner to have a very low "water" content which was difficult to measure accurately, but was certainly less than 0.01%. N_2O_4 distilled in this way will be described throughout this report as 'dry N_2O_4'.

4. SOLUTIONS OF $Fe(NO_3)_3xN_2O_4$ IN 100% HNO_3

(i) Preparation of 100% HNO_3

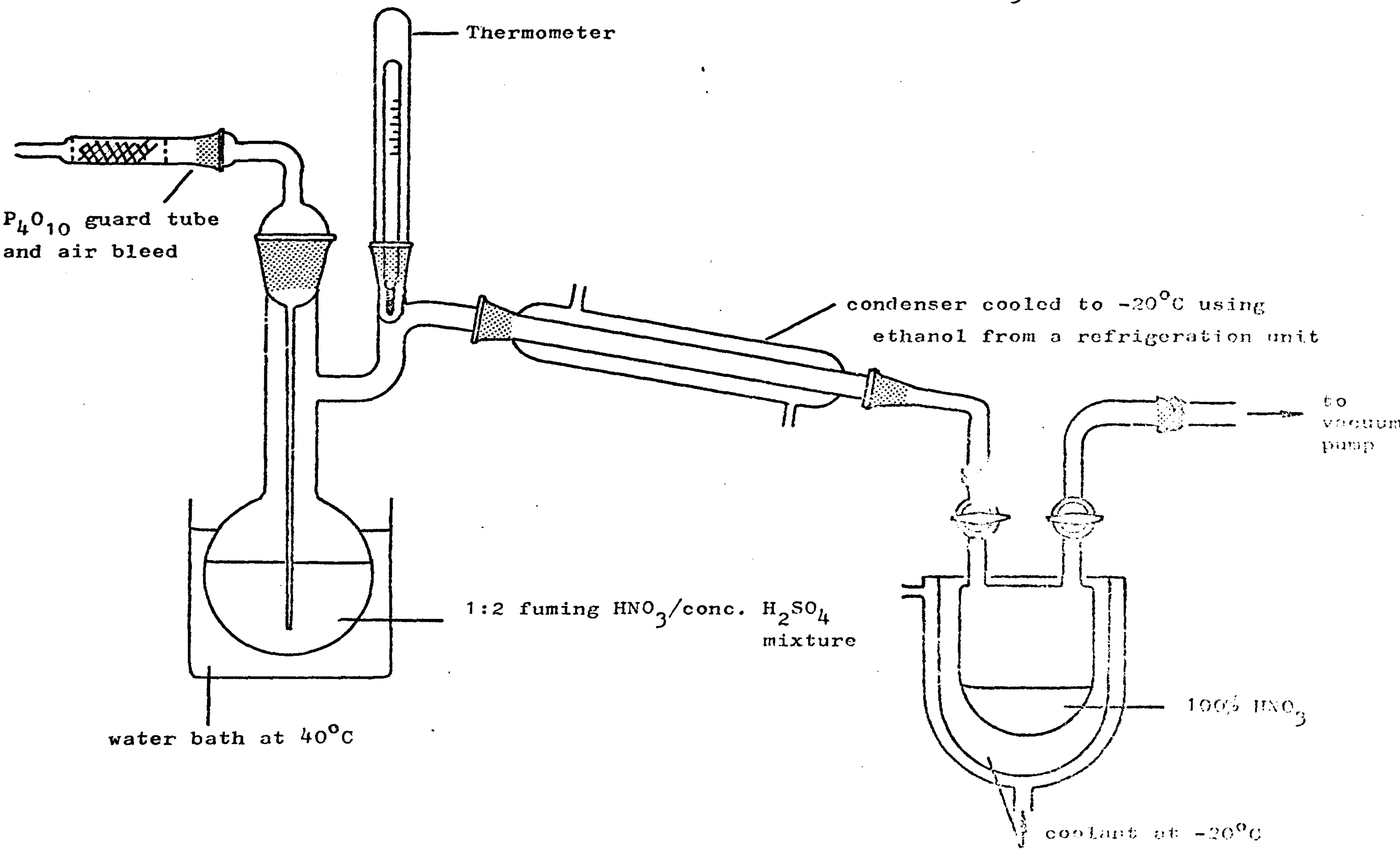
100% nitric acid is prepared using the apparatus illustrated in Fig. 4.1. A mixture of fuming HNO_3 and concentrated H_2SO_4 (1:2) is heated to 40°C (10^{-2}mm) at which temperature 100% HNO_3 distils into the receiver. Yields are improved if both the condenser and receiver are cooled to -20°C.

The 100% acid behaves as a mixture of the free acid, acid anhydride and water in accordance with the equilibrium

$$2HNO_3 \rightleftharpoons N_2O_5 + H_2O \quad (N_2O_5 \text{ ionised to } NO_2^+ \text{ and } NO_3^-)$$

for which several lines of physical evidence are available.[19] The reagent has been used with little success in the preparation of anhydrous nitrates and its reactions with the anhydrous chlorides $CrCl_2$, $CrCl_3$, $MnCl_2$, $FeCl_2$, $FeCl_3$, $CoCl_2$, $NiCl_2$, and $CuCl_2$ produce only hydrated nitrates.[20] In spite of this, 100% HNO_3 has been used with success in these laboratories in the recrystallization of anhydrous nitrate complexes, e.g. $NO_2^+Au(NO_3)_4^-$ and $K^+Au(NO_3)_4^-$.[21] Since nitric acid is one of the contaminants of propellant N_2O_4 which may be responsible for the production of the flow-decay material, it was of interest to examine the nature of $Fe(NO_3)_3xN_2O_4$ in 100% nitric acid. This adduct forms apparently stable brown solutions in 100% HNO_3 and the infra-red and Raman spectra of such solutions were recorded in order to ascertain the species present. Before discussion of these spectra, however, it is relevant to consider briefly the infra-red and Raman spectra of 100% HNO_3 itself.

Figure 4.1 Apparatus for the preparation of 100% HNO_3



(ii) Vibrational spectroscopy of 100% HNO_3

The infra-red spectrum of 100% HNO_3 was recorded on a Perkin-Elmer 457 spectrometer using a specially designed Kel-F solution cell fitted with silver chloride windows separated by a Teflon spacer (ca 10μ). The Raman spectrum was recorded on a Cary 81 spectrophotometer using a Spectra-Physics 125 He-Ne Laser as an excitation source (output approx. 60mW at 632.8 nm). Samples for Raman spectroscopy were contained in glass capillary cells (ca 1 mm i.d.) and were filled and sealed in a dry-box. Depolarisation ratios were determined by observing the spectrum with the plane of the polarised incident light parallel and perpendicular, respectively, to the axis of the polaroid analyser. The values were not obtained directly, but the sample cell was calibrated using accurately knownstandards.

The bands attributable to 100% nitric acid are listed in Table 4.1 and are illustrated in Figs. 4.2 (infra-red) and 4.3 (Raman). The infra-red spectrum is as expected for a unidentate covalent nitrate and is accordingly assigned in the C_s point group. A point of particular interest is the appearance of bands at 2365 and 2355 cm^{-1} which can be assigned to the antisymmetric stretching vibration of the nitronium ion (NO_2^+). This has been observed by earlier workers[22] and provides evidence for the self-ionisation of the acid. The associated NO_3^- band would be expected at ca 830 cm^{-1} but is invariably weak and is not observed in this case.

The Raman spectrum of 100% nitric acid is again as expected for a unidentate covalent nitrate. It is similar to the spectrum reported by earlier workers[23] and provides further

Table 4.1.

Vibrational spectrum of HNO_3

Infra-red (cm^{-1})	Raman (cm^{-1})	Assignment
3900 m		
3250 vs,vb		v_7 O-H stretch
2600 sh		
2365 m,sp		
2355 sh		
1670 vs,br	1683 w,dp	v_4 NO_2 asymm. stretch
	1539 w	2 x v_6
	1400 w	NO_2^+ symm. stretch
1300 vs, vb	1308 vs, p	v_1 NO_2 symm. stretch
	1058 w	NO_3^- (NO stretch)
920 vs,b	929 vs,p	v_2 N-OH stretch
765 s		v_6 out of plane bend
700-400 vs,vb	681 s,p	v_3 NO_2 bend
	614 m,dp	v_5 N-OH bend

v, very; s, strong; m, medium; w, weak; sh, shoulder; sp, sharp; b, broad; p, polarised; dp, depolarised.

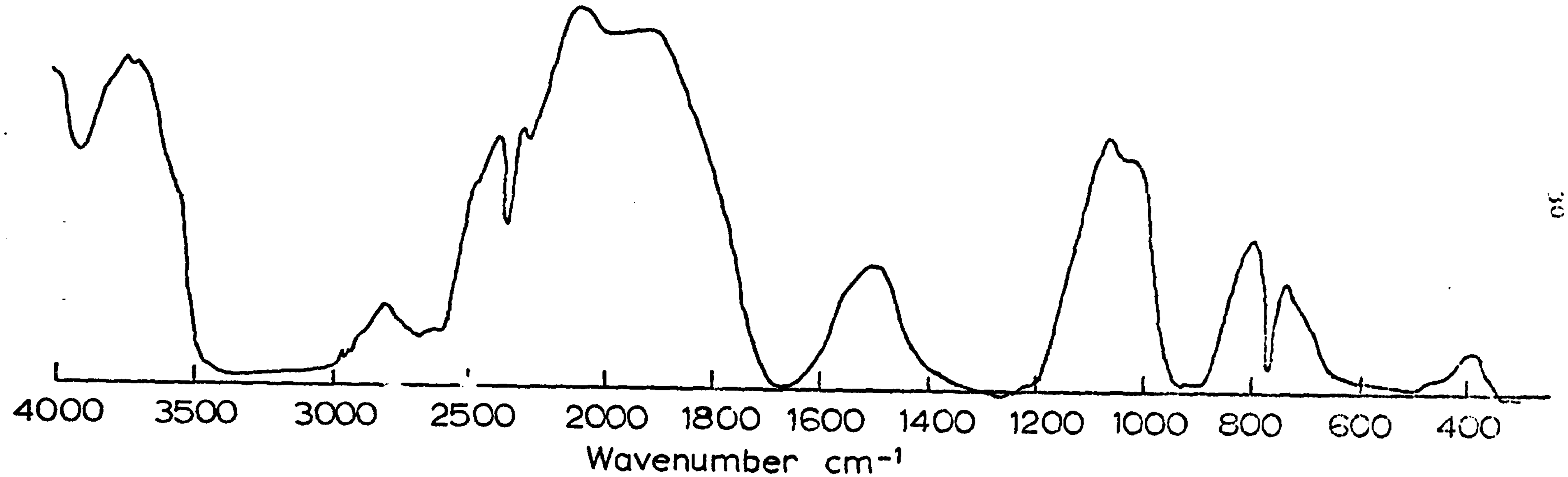


Figure 4.2 I.R. spectrum of HNO_3

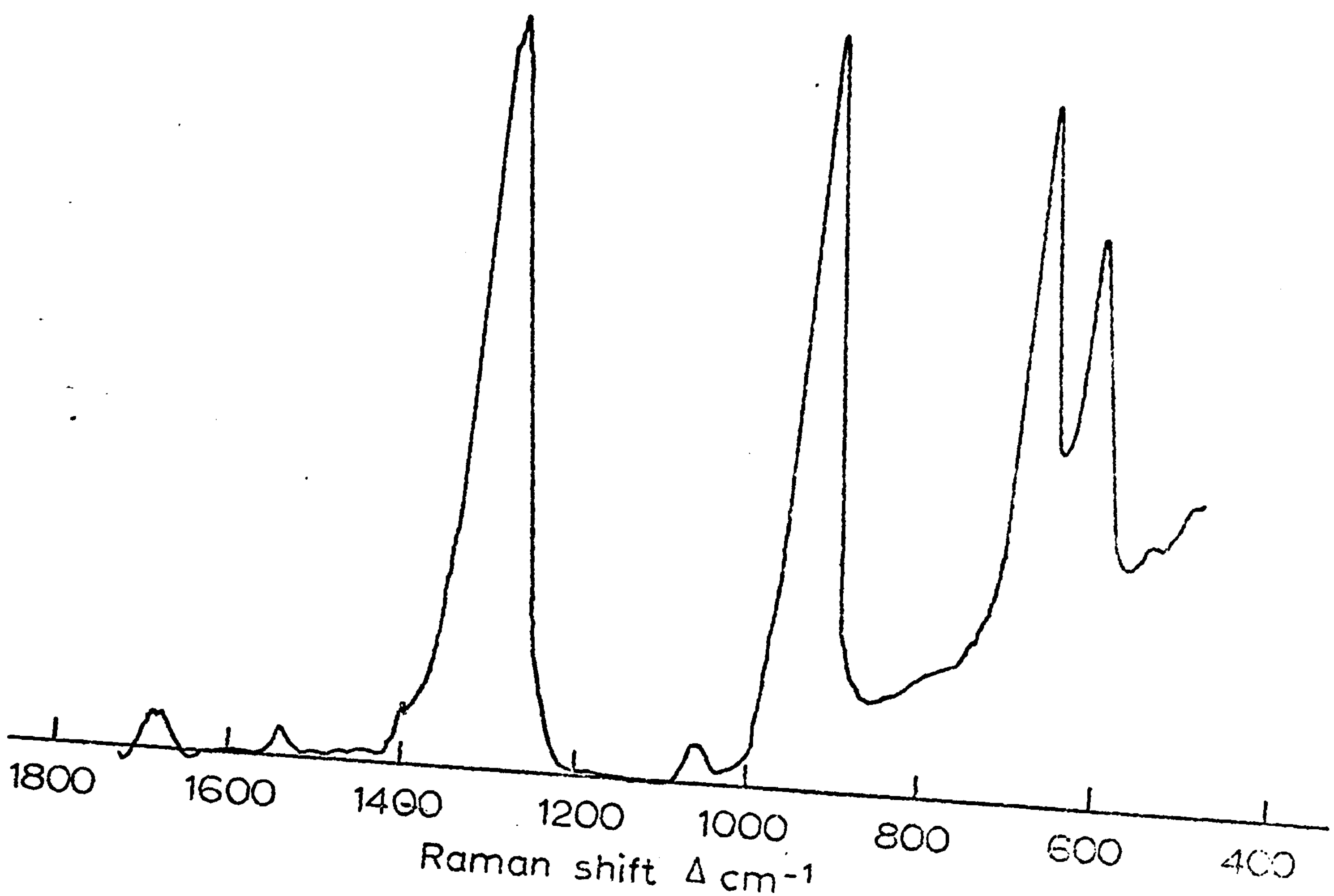


Figure 4.3 Raman spectrum of HNO_3

evidence for the self-ionisation of the 100% acid. Weak bands observed at 1400 and 1058 cm^{-1} are characteristic of NO_2^+ (symmetric stretch) and NO_3^- (N-O stretch) respectively and can be varied in intensity by adding species which repress the self-ionisation of HNO_3. For example, addition of very small quantities of water to the 100% acid diminishes the intensity of both the 1400 and 1058 cm^{-1} bands. Further addition of water allows the normal ionisation of the dilute acid to proceed. When NO_2^+ is added to the pure acid, the 1058 cm^{-1} band disappears and similarly the 1400 cm^{-1} band disappears if nitrate ion is added.[23]

(iii) Vibrational spectroscopy of solutions of $Fe(NO_3)_3xN_2O_4$ in 100% HNO_3

The bands attributable to $Fe(NO_3)_3xN_2O_4$ in 100% HNO_3 are listed in Table 4.2 and are illustrated in Figs. 4.4 (infra-red) and 4.5 (Raman). The bands in both spectra are consistent with the presence of a covalent nitrato-species of iron which may be identified with some confidence. The bands in the covalent nitrate region are virtually identical with those found for the solid $Fe(NO_3)_3.N_2O_4$ (see Table 2.1 and Fig. 2.1). As mentioned in Section 2(iii), this is known to contain the dodecahedral anion $Fe(NO_3)_4^-$, in which four bidentate nitrate groups are symmetrically disposed around iron(III).

Strong evidence for the formation of $Fe(NO_3)_4^-$ ions from $Fe(NO_3)_3xN_2O_4$ dissolved in 100% HNO_3 has therefore been obtained and the stretching frequency of the expected NO^+ counter ion is also observed (2295 cm^{-1}). The shoulder on this band at 2240 cm^{-1} may be indicative of the persistence in HNO_3 solution of NO^+ ligation by the excess N_2O_4 (or NO_2) implied

Table 4.2.

Vibrational spectrum of $Fe(NO_3)_3 xN_2O_4$ in 100% HNO_3 solution

Infra-red (cm^{-1})	Raman (cm^{-1})	Assignment
2295 s	2298 m	NO^+ stretch
2240 sh		NO^+ stretch
	1605 ms,p	ν_1 N-O stretch
	1250 w,dp	ν_4 NO_2 asymm. stretch
1010 s,b	1028 ms,p	ν_2 NO_2 symm. stretch
795 s,sp	785 m	ν_6 out of plane bend

s, strong; sh, shoulder; sp, sharp; b, broad;

m, medium; w, weak; p, polarised; dp, depolarised.

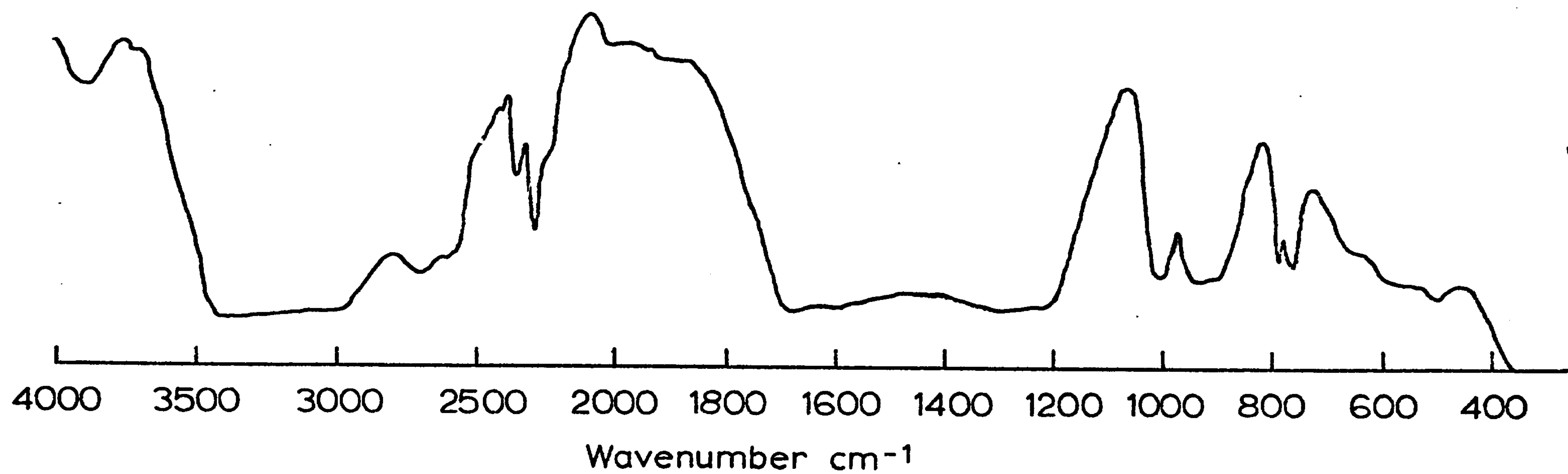
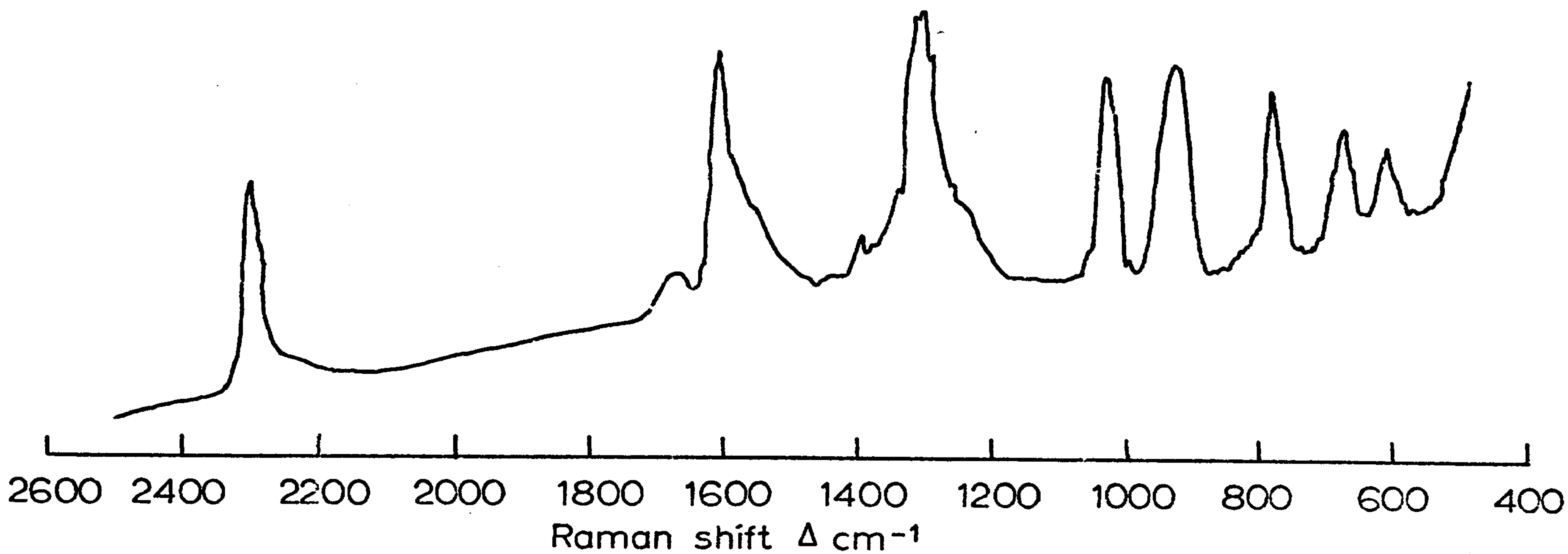


Figure 4.4 I.R. spectrum of a solution of $Fe(NO_3)_3xN_2O_4$ in HNO_3

Figure 4.5

Raman spectrum of a solution of

$Fe(NO_3)_3 xN_2O_4$ in HNO_3



in the formula $Fe(NO_3)_3xN_2O_4$, as proposed earlier for solids (Section 2(iii)). No change in the Raman spectrum of $Fe(NO_3)_3xN_2O_4$ in 100% HNO_3 was observed over a period of 24 hours confirming the high stability of the above ionic species in this medium.

The further spectroscopic method for identifying the mode of coordination of nitrate groups in solution species, referred to in Section 2(iii) b) requires measurement of the depolarisation ratios of the three bands assigned to stretching fundamentals (at ca 1600, 1200, 1000 cm^{-1}) in the Raman spectrum.[15] The polarisation sequences predicted for unidentate and bidentate nitrate groups are as follows:

Band (cm^{-1})	1600	1200	1000
Unidentate (C_{2v})	dp	p	p
Bidentate (C_{2v})	p	dp	p.

p = polarised, dp = depolarised

The polarisation sequence observed for $Fe(NO_3)_3xN_2O_4$ in 100% HNO_3 is p, dp, p which indicates that the anion $Fe(NO_3)_4^-$ in HNO_3 solution still contains nitrate groups bonded in a bidentate fashion.

When $Fe(NO_3)_3xN_2O_4$ is dissolved in 100% HNO_3, the band observed at ca 1050 cm^{-1} in the pure acid disappears, whereas the band at 1400 cm^{-1} shows a marginal increase in intensity. A possible cause of this is the partial oxidation of NO^+ to NO_2^+ which then causes a suppression of the self-ionisation of the acid.

5. BEHAVIOUR OF $Fe(NO_3)_3xN_2O_4$ IN HNO_3/N_2O_4 MIXTURES

(i) HNO_3/N_2O_4 phase diagram

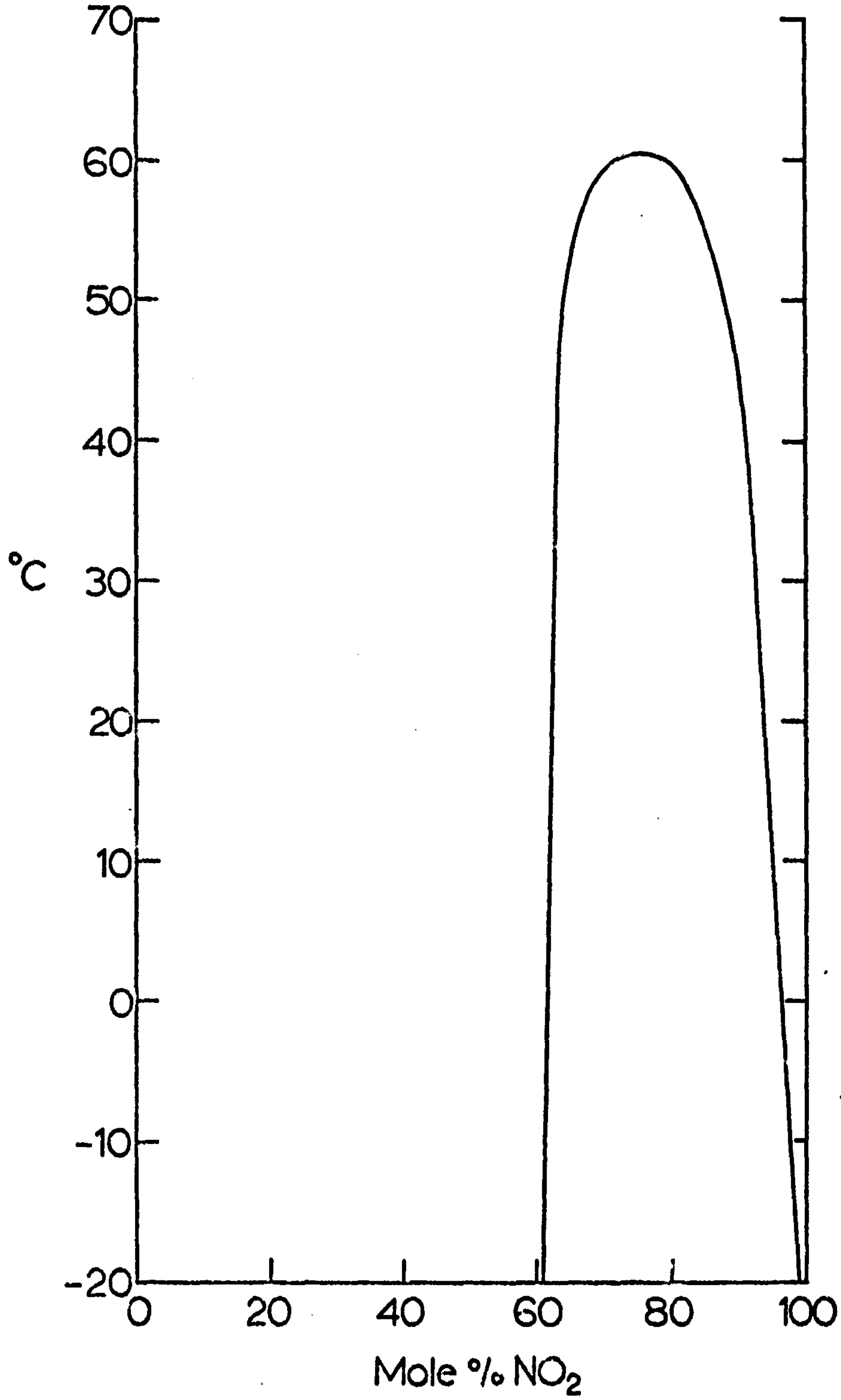
The HNO_3/N_2O_4 phase diagram [24,25] is illustrated in Fig. 5.1. The points of relevance to the study of flow decay problems are: I. A relatively small amount of nitric acid of about 7 wt % at 25°C is sufficient to give rise to a second phase. This amount of nitric acid may be expressed as about 1.2 wt % water. II. The second phase which is formed on gradual addition of nitric acid to N_2O_4 contains almost all of the nitric acid and consists of about 46 wt % of nitric acid at 25°C. III. The slope of the mutual miscibility curve is large. A concentrated homogeneous solution of HNO_3 in N_2O_4 at 30°C, if cooled to 20°C, would give about 5% of a second phase, containing 46 wt % of HNO_3.

Experiments described below (Section 5(ii) b)) indicate that the nitric acid-rich phase has a greater density than the N_2O_4 rich phase.

(ii) Effect of $Fe(NO_3)_3xN_2O_4$ on the HNO_3/N_2O_4 phase system

a) General considerations

$Fe(NO_3)_3xN_2O_4$ is very soluble in nitric acid (See Section 4(iii), above), and virtually insoluble in N_2O_4.[1] Also there is spectroscopic evidence (Section 4(iii)) that $Fe(NO_3)_3xN_2O_4$ is ionised in nitric acid as $Fe(NO_3)_4^-$ and NO^+. These considerations, and the simplicity of the HNO_3/N_2O_4 phase diagram, make it seem likely that behaviour analogous to the water-ether-inorganic salt system might occur: a high affinity of the salt for water, and



HNO_3/N_2O_4 phase diagram.

Figure 5.1

hence of water for the salt lowers the solubility of the ether in the water. The ether is therefore "salted out" from the aqueous phase. Likewise, the addition of a highly nitric acid-soluble material (i.e. $Fe(NO_3)_3xN_2O_4$) to an HNO_3/N_2O_4 mixture was expected to bring about the separation of a second phase containing a large amount of nitric acid.

b) Experimental study

Fuming nitric acid was dropped into stirred N_2O_4 at 15^oC, and the fate of each drop observed with a low-power microscope. About 5 ml of nitric acid could be added to 80 ml N_2O_4 before the separation of a second phase occurred. When separation did occur, the second phase was denser than the bulk N_2O_4. The globules which formed showed little tendency to agglomerate or to adhere to the (glass) walls of the flask.

A solution of $Fe(NO_3)_3xN_2O_4$ in fuming nitric acid (ca 40 mg/ml) was then dropped into 80 ml dry N_2O_4, with stirring, at ca 10^oC. On the addition of only one drop of the solution a second phase was formed, which did not fully dissolve on stirring, but adhered to the glass, with a small contact angle. This contact angle increased over about 20 minutes, while maintaining stirring, and the second phase still adhered tenaciously to the side of the flask. Several more drops were added, and these showed similar behaviour. After one day the viscosity of the drops had increased to a maximum (they were no longer moved by the motion of the magnetic stirrer) and were stable under these conditions for over a week. After decantation of the top

phase, the lower phase was treated with a slow stream of dry nitrogen until there was no immediately visible NO_2 evolved on allowing to stand. The I.R. spectrum of the resulting clear, pale brown, viscous liquid was then recorded (sample between AgCl plates). The spectrum indicated the presence of HNO_3, NO^+ (broad band), and $Fe(NO_3)_4^-$. Bands typical of molecular N_2O_4 were absent (See Section 2(iii)). On addition of dry liquid N_2O_4 (ca 40 ml) to this viscous liquid (ca 20 mg) complete conversion to a dark brown solid occurred in about 2 hours. The I.R. spectrum (Nujol mull/AgCl) of the brown solid was consistent with its being $Fe(NO_3)_3xN_2O_4$.

(iii) Spectroscopic studies of $Fe(NO_3)_3xN_2O_4$ in HNO_3/N_2O_4 mixtures

a) Preliminary investigations

On account of the experiments described above, attention has been focussed on the denser, nitric acid-rich phase of the HNO_3/N_2O_4 system, and solutions of $Fe(NO_3)_3xN_2O_4$ in this mixture. The results now described were obtained before the development of an appropriate I.R. cell. The characteristic I.R. spectrum of solutions of N_2O_4 in HNO_3 (Fig. 5.2) and of solutions of $Fe(NO_3)_4xN_2O_4$ in HNO_3/N_2O_4 mixtures (Fig. 5.3) were obtained between 4000 cm^{-1} and 1000 cm^{-1} using a cell which consisted of CaF_2 windows separated by a PTFE spacer. This assembly was filled with the solution in a dry box and was firmly clamped. A solution of $Fe(NO_3)_3xN_2O_4$ in HNO_3 containing some N_2O_4 was obtained by adding $Fe(NO_3)_3xN_2O_4$ to the two phase HNO_3/N_2O_4 mixture, and taking a sample of the lower phase.

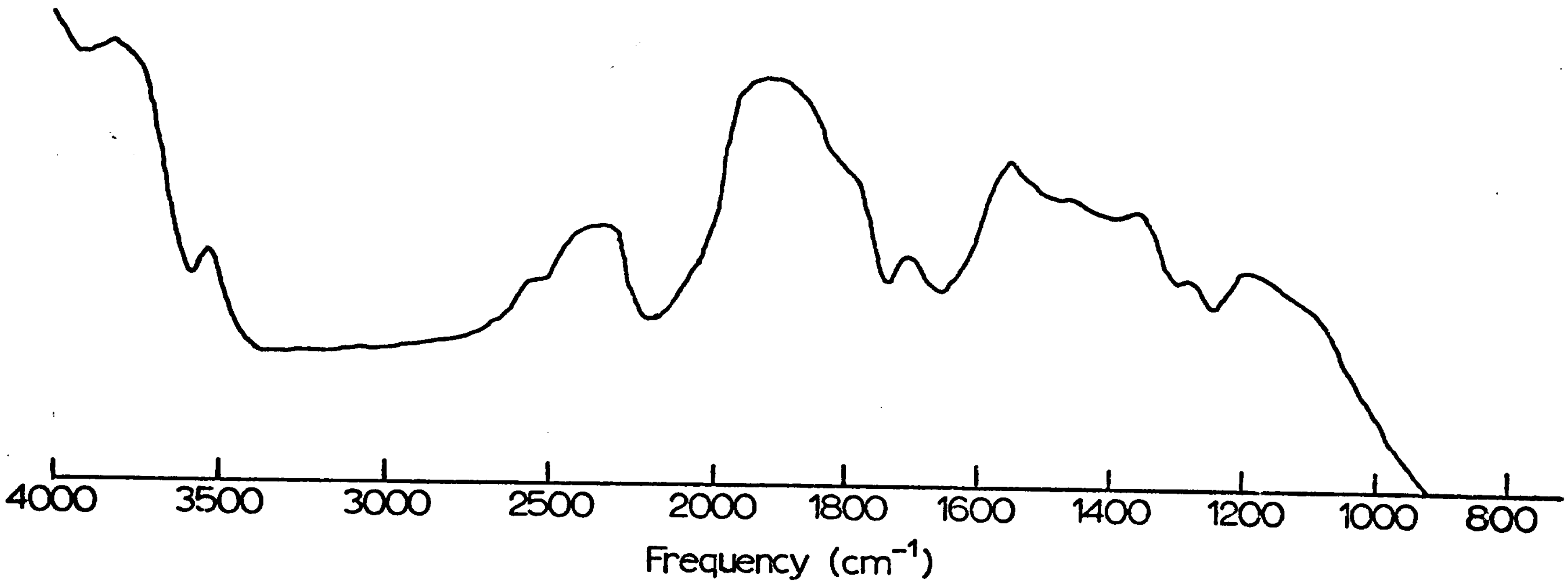


Figure 5.2 **I.R. spectrum of solution of N_2O_4 in HNO_3**

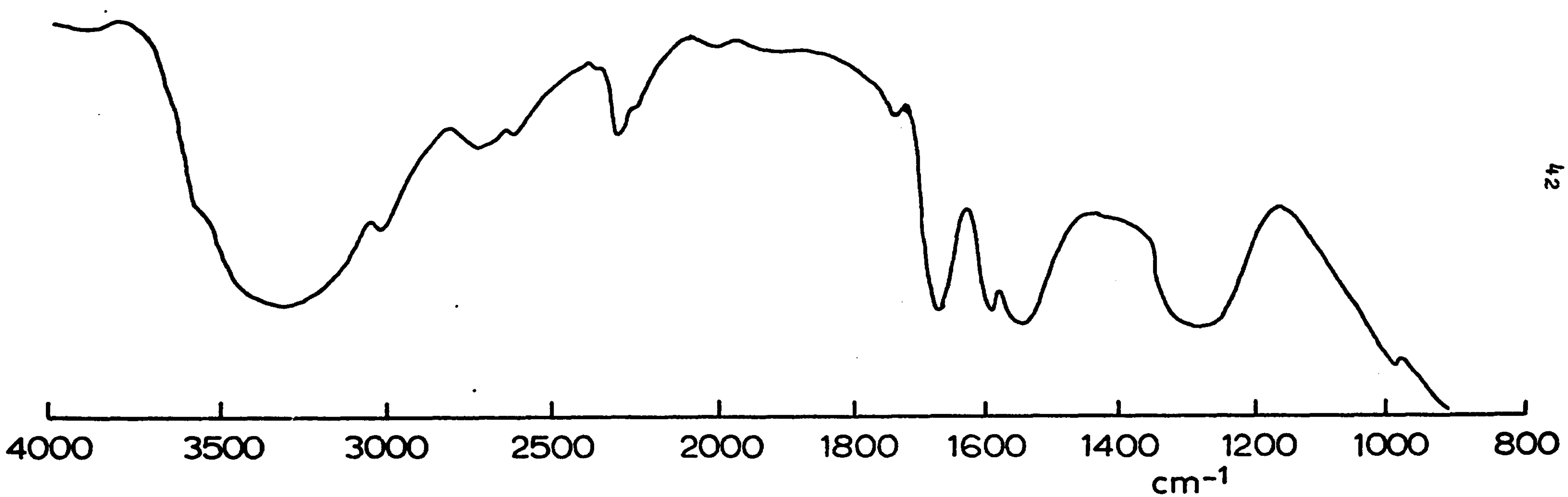


Figure 5.3 Typical I.R. spectrum of $Fe(NO_3)_3xN_2O_4$ in HNO_3 containing N_2O_4

The I.R. spectrum of the solution of N_2O_4 in HNO_3 (Fig. 5.2) shows the characteristic HNO_3 bands (see Section 4(ii)) and the bands attributable to molecular N_2O_4.[8] A broad band at about 2220 cm^{-1} is also seen. This has been observed in Raman studies of HNO_3/N_2O_4 mixtures[12,13] and attributed to the ion $N_2O_3^+$, which may be considered as a nitrosonium ion ligated by NO_2, thus lowering the absorption frequency below the value close to 2300 cm^{-1} for "free" NO^+.[26]

The I.R. spectrum of the solution of $Fe(NO_3)_3xN_2O_4$ in HNO_3 containing some N_2O_4 is shown in Fig. 5.3. Bands typical of HNO_3 and N_2O_4 are seen. The remainder of the spectrum shows the characteristic bands of $Fe(NO_3)_4^-$ (1600 cm^{-1}, 1550 cm^{-1}, 1000 cm^{-1}), an NO^+ band at 2300 cm^{-1}, and also the broad band at 2220 cm^{-1}, assigned above. The relative intensities of the 2300 cm^{-1} and 2220 cm^{-1} bands varied with the concentration of N_2O_4 in the solution.

b) <u>Projected spectroscopic studies</u>

Raman spectral studies of $Fe(NO_3)_3xN_2O_4$ in HNO_3 (Section 4(iii)) will be extended to solutions of $Fe(NO_3)_3xN_2O_4$ in HNO_3 containing various amounts of N_2O_4, in order to study the influence of N_2O_4 on the appearance of the spectrum in the NO^+ region. Other $Fe(NO_3)_3xN_2O_4/HNO_3/N_2O_4$ systems of interest spectroscopically are the viscous materials whose preparation is described in Section 5(iv) below.

Complementary I.R. studies are now possible as a suitable Kel-F cell with AgCl windows has been developed (see Section 4(iii)).

(iv) <u>Extraction of solutions of $Fe(NO_3)_3xN_2O_4$ in HNO_3 by N_2O_4</u>

The qualitative study described in Section 5(ii) b) indicated that a viscous HNO_3 solution of $Fe(NO_3)_3xN_2O_4$ had considerable stability in contact with a large amount of N_2O_4, and that this HNO_3 phase was, however, converted to a solid on further treatment with dry N_2O_4. In order to place these observations on a more quantitative basis, a series of experiments has been carried out in which solutions of $Fe(NO_3)_3xN_2O_4$ in HNO_3 were submitted to progressive extraction of the nitric acid by dry N_2O_4, either batch-wise or continuously in a liquid-liquid extractor designed for this purpose.

a) <u>Batch-wise extraction</u>

0.68 g $Fe(NO_3)_3.N_2O_4$ and 14.43 g 97% nitric acid were placed in a Schlenck tube fitted with a PTFE tap. A weighed amount of dry N_2O_4 (<u>ca</u> 50 g) was added to the nitric acid phase against a countercurrent of N_2 and the system allowed to equilibrate (i.e. until the proportions of the two phases did not change). The upper phase was then decanted as completely as possible through the PTFE tap and the remainder was removed by means of a stream of dry N_2. The lower phase was weighed and its appearance noted. This process was repeated with a further seven portions of N_2O_4. The results are presented in Table 5.1.

The salient features of these results are:

I. The presence of 0.7 g $Fe(NO_3)_3.N_2O_4$ in 14 g HNO_3 lowers the solubility of N_2O_4 in the nitric acid from about 14 g to about 8 g.

Table 5.1

Batch-wise extraction of $Fe(NO_3)_3.N_2O_4$ in HNO_3 by dry N_2O_4

After Extraction No.	Approx. time to equil--ibrate	Wt. of lower phase (g)	Wt. of N_2O_4 last added (g)	Wt. of top phase removed (g)	Appearance of lower phase
0	-	15.11	-	-	Clear mobile solution
1	5 min	22.98	58.00	50.13	"
2	20 min	12.52	55.45	65.91	"
3	40 min	6.11	55.89	62.30	"
4	16 hr	1.54	57.79	62.36	Dark red/brown, viscous. Did not adhere strongly to glass.
5	16 hr	1.32	65.49	65.71	Dark brown, very viscous Adhered strongly to glass
6	16 hr	1.05	56.72	56.99	Dark brown solid
7	16 hr	0.94	67.04	67.15	"
8	5 days	0.79	ca200	-	"

II. The second and subsequent extractions progressively decrease the lower phase weight.

III. The lower phase ultimately solidifies, and the weight of the product is about 10% greater than that of the $Fe(NO_3)_3.N_2O_4$ starting material.

The properties of solids obtained by extraction procedures are discussed in Section 5(v) below.

b) Continuous extraction

A series of experiments carried out with a liquid-liquid extractor (Fig. 5.4) were performed to verify the qualitative results of the batch-wise extraction, to allow intermittent monitoring of the water content of the upper (N_2O_4) phase by ^1H n.m.r. (technique described in Section 3(iii)), and to facilitate the production of solids and viscous liquids in $Fe(NO_3)_3.N_2O_4/HNO_3/N_2O_4$ systems.

$Fe(NO_3)_4.N_2O_4$ and 100% HNO_3 were weighed into tube A (Fig. 5.4) and the apparatus was assembled as drawn. Distillation of N_2O_4 occurred without heating, but a convenient rate of distillation could be obtained by gentle heating of the flask B. When a sample of the top phase was required for ^1H estimation, distillation was discontinued and the top half of the inner funnel C removed to allow the lower phase to achieve equilibrium with a homogeneous upper phase. When the phase boundary in the sample tube A no longer fell, a sample of the top phase was transferred to an n.m.r. tube as rapidly as possible by means of a pipette and the tube was sealed.

Several experiments have shown that a solution of ca 2 g $Fe(NO_3)_4.N_2O_4$ in ca 10 g 100% HNO_3 will dissolve about

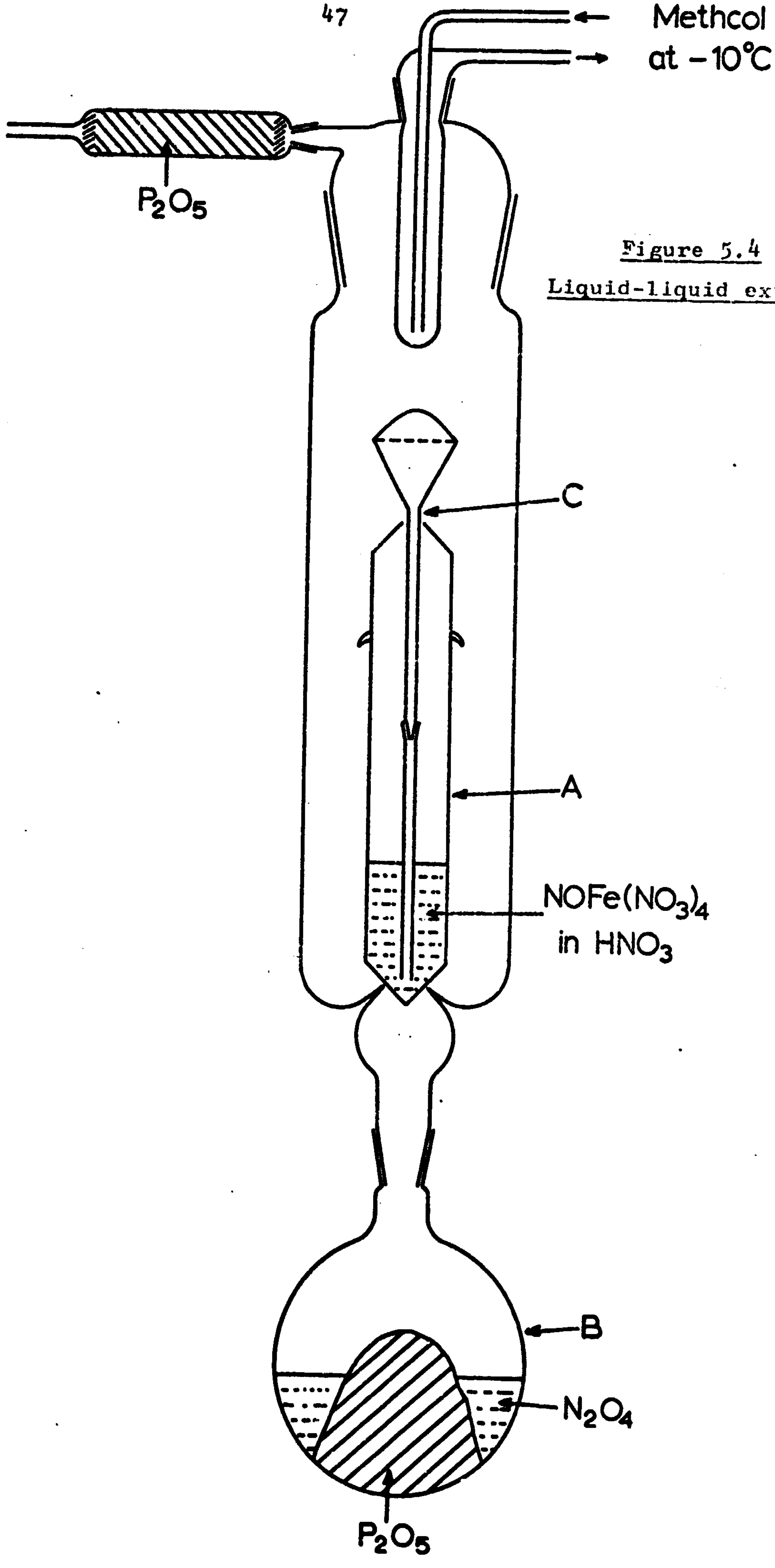


Figure 5.4
Liquid-liquid extractor

50% of its volume of N_2O_4 before a second less dense phase separates. Higher concentrations of $Fe(NO_3)_3.N_2O_4$ limit the solubility of N_2O_4 in the HNO_3 phase even further.

A sample of the viscous lower phase was, in one experiment, removed from the apparatus a short time prior to solidification. On treatment with water it effervesced, evolved NO_2, and was totally soluble.

In another experiment an attempt was made to isolate a sample of the viscous lower phase. The upper phase (0.07% water, estimated by ^1H n.m.r.) was decanted off, but it was observed with interest that the lower phase immediately solidified.

In a further experiment the appearance of the lower phase was noted as a function of the "water" content of the upper phase on progressive extraction. The system was allowed 24 hours to come to equilibrium before each sample of the upper phase was taken for quantitative examination by ^1H n.m.r. The results are recorded in Table 5.2.

Table 5.2

Continuous extraction of $Fe(NO_3)_3xN_2O_4$ in HNO_3 by dry N_2O_4

Sample	% "water" content of upper phase	Lower phase appearance
1	0.6	Clean, red/brown mobile liquid
2	0.24	"
3	0.15	"
4	0.13	"
5	0.12	Increased viscosity
6	0.12	Extremely viscous liquid
7	0.17	Solid

The possibility that equilibrium between a given sample of the upper phase and the lower phase was not achieved in 24 hours must be recognised. It can be seen, however, from Table 5.2 that a progressive diminution in the "water" content of the upper phase was noted as extraction proceeded under the above conditions with the exception of sample 5 which showed an anomalously high value. This may be an indication that equilibrium was not being achieved. A pronounced increase in the "water" content of the upper phase (sample 7) occurred on separation of solid, presumably as a result of expulsion of nitric acid from the liquid phase on solidification. It is noteworthy that this solid was then stable in contact with N_2O_4 of "water" content as high as 0.17%.

Further experiments using the liquid-liquid extractor are in progress, and further attempts will be made to isolate and characterise the viscous lower phase.

c) <u>The stability of gels in the $Fe(NO_3)_3xN_2O_4/HNO_3/N_2O_4$ system - projected work</u>

In view of the rather long times necessary to allow equilibration during the 'continuous' extraction technique, and the difficulty of ensuring that equilibrium was reached, experiments are planned whereby mixtures of $Fe(NO_3)_3xN_2O_4$, HNO_3 and N_2O_4 will be sealed in n.m.r. tubes. The "water" content of the top phase may then be monitored as a function of time, the appearance of the lower phase observed as a function of time, and the appearance of the lower phase noted as a function of the "water" content of the upper phase with which it is in (true) equilibrium.

(v) Solids produced from extraction experiments

In every experiment so far performed, the extraction of $Fe(NO_3)_3xN_2O_4$ in HNO_3 with dry N_2O_4 ultimately led to the formation of a solid. In one experiment a solid was produced whose X-ray powder pattern was identical to that for the starting material - i.e. $Fe(NO_3)_3.N_2O_4$ produced from $FeCl_3/EtOAc/N_2O_4$ (See Table 2.2(c)).

The solids were all dark brown, and showed a tendency to evolve NO_2. Samples which had been treated with a gentle stream of dry N_2 were lighter in colour and showed less tendency to evolve NO_2 than those where the solid was isolated by decantation only.

a) Infra-red spectra

A typical spectrum is shown in Fig. 5.5, obtained as a nujol mull between AgCl plates. The bands at 2930 cm^{-1}, 2860 cm^{-1}, 1460 cm^{-1} and 1380 cm^{-1} are nujol absorptions.

The remainder of the spectrum is very similar to that for $Fe(NO_3)_3xN_2O_4$, $x > 1$ (See Section 2(iii)). The main features of interest are the NO^+ region (2200-2300 cm^{-1}) and the absence of nitric acid. The relative intensities of the band at 2300 cm^{-1} and the broad band centred at 2220 cm^{-1} varied from sample to sample, and in some cases no 2300 cm^{-1} ('free' NO^+) band was observed. Although not evident in Fig. 5.5, weak bands assignable to the most intense absorptions of HNO_3 were seen in some cases. No evidence for any iron-containing species other than $Fe(NO_3)_4^-$ was found.

b) Analysis

The following analytical methods were employed:-

Fe The atomic absorption method described in Section 2(ii) c) was used.

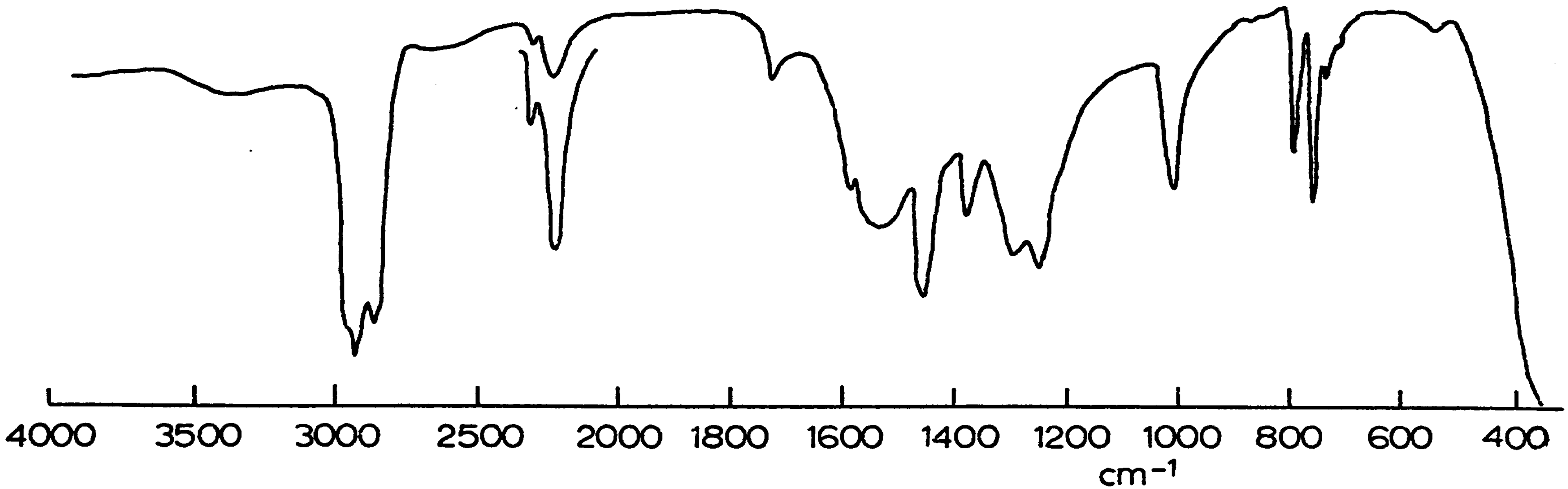


Figure 5.5

Typical I.R. spectrum of solid extraction product of $Fe(NO_3)_3xN_2O_4$ in HNO_3 by N_2O_4

$\underline{N_2O_4 \text{ content}}$ Two methods were used to obtain N_2O_4 content, each using the technique of sealed bottle hydrolysis in aqueous alkali (described in Section 2(ii)), followed by estimation of NO_2^- produced.

Estimation of nitrite by u.v. spectroscopy[27] was attractive, as the method could potentially give a direct estimation of nitrate, and hence total nitrogen, as well as nitrite. However, very high results both for nitrate and nitrite were invariably obtained by this method, and in some cases the solutions were visibly yellow. Both effects were attributed to the presence of soluble hydroxo-iron(III) species ("ferrites"), the u.v. absorption of which would augment that due to nitrate and nitrite. The alkali concentration used for the hydrolysis of the solid was therefore varied, in the hope that conditions might be found under which complete precipitation of iron as hydroxide/ hydrated oxide would occur. However, no conditions, which gave chemically reasonable or reproducible results, could be found.

The method eventually used for determination of N_2O_4 content was that described in Section 2(ii) b). This was found to be quite satisfactory.

The analytical results for several solids obtained by extraction experiments (Section 5(iv)) indicated compositions $Fe(NO_3)_3xN_2O_4$ where x = 1.0 - 1.5. For each solid, the Fe content gave a higher value of x than the NO_2^- determination but the atomic absorption method for Fe was of significantly lower accuracy than the titration of NO_2^- by Ce^{IV}.

Instrumental improvements will allow future Fe

determinations to be carried out with comparable accuracy to the NO_2^- analysis.

c) <u>"Water" content of solids</u>

If "water" estimation on solids becomes necessary, a quantitative ^1H n.m.r. procedure may be applicable. $Fe(NO_3)_3.N_2O_4$ is highly soluble in $MeNO_2$, and the solutions may be amenable to estimation by ^1H n.m.r., possibly using the protons of $MeNO_2$ to provide a locking signal.

Difficulties may arise from line broadening in the presence of high concentrations of paramagnetic iron(III) species (d^5, high spin in $Fe(NO_3)_4^-$) and the selection of suitable standards will also pose problems. Nevertheless, the potentialities of the method will be examined.

d) <u>The stability of solids in the $Fe(NO_3)_3xN_2O_4$/HNO_3/N_2O_4 system - projected work</u>

The work described in 5(iv) indicates that $Fe(NO_3)_3xN_2O_4$ remains a solid in the presence of N_2O_4 containing small amounts of HNO_3 (0.17% "water" content). However, equilibration is apparently slow, and the technique described in connection with the "continuous" extraction experiments is not ideal for determination of the limiting "water" content of N_2O_4 necessary for stability of the solid. This will be studied in the manner proposed for examination of the stability of gels in these systems (Section 5(iv) c)).

(vi) <u>Rationalisation of the behaviour of $Fe(NO_3)_3xN_2O_4$ in HNO_3/N_2O_4 mixtures</u>

In summary, the main features of the work described in Sections 4 and 5 are:

I. $Fe(NO_3)_3xN_2O_4$ dissolves in 100% HNO_3 and HNO_3/N_2O_4 mixtures to give NO^+, a modified NO^+ ion (probably $N_2O_3^+$),

and $Fe(NO_3)_4^-$.

II. Treatment of a solution of $Fe(NO_3)_3xN_2O_4$ in HNO_3 with dry N_2O_4 leads ultimately to the recovery of a solid $Fe(NO_3)_3xN_2O_4$ from the solution.

III. Solutions of HNO_3 in N_2O_4 have been prepared where the concentration of HNO_3 is too small for the $Fe(NO_3)_3xN_2O_4$ to separate out a liquid, HNO_3-rich phase.

IV. $Fe(NO_3)_3xN_2O_4$ is stable in contact with N_2O_4 containing a small amount of HNO_3 and is not converted, for instance, into a hydrated nitrate or hydroxy species.

At this time, it appears most fruitful to interpret the properties of the $Fe(NO_3)_3xN_2O_4/HNO_3/N_2O_4$ system in terms of a gross modification of the HNO_3/N_2O_4 phase diagram by the $Fe(NO_3)_3xN_2O_4$. The observed behaviour is qualitatively that expected for any ionic salt in the HNO_3/N_2O_4 system. The ionisation to NO^+ and $Fe(NO_3)_4^-$(I) and the lack of chemical reaction except for strong ligation of NO^+ is consistent with this idea. Points II, III and IV above are also consistent with this model, since at a suitably low HNO_3 content in the HNO_3/N_2O_4 system only one liquid phase is obtained and it is likewise expected that below some critical HNO_3 content in a $Fe(NO_3)_3xN_2O_4/HNO_3/N_2O_4$ system, only one liquid phase would again be obtained - i.e. $Fe(NO_3)_3xN_2O_4$ would remain a solid.

6. PROJECTED INVESTIGATIONS

(i) Dissociation vapour pressures of the $Fe(NO_3)_3xN_2O_4$ system

a) Relevance of these studies

The work described in Section 2 indicated the propensity of $Fe(NO_3)_3.N_2O_4$ i.e. $NO^+Fe(NO_3)_4^-$ for retention of further N_2O_4 which results in the modification of the vibrational spectrum and X-ray powder pattern, and the stabilisation of crystalline form. The type of interaction whereby the additional N_2O_4 is retained and the possible existence of stable adducts between $Fe(NO_3)_3$ and N_2O_4 other than the 1:1 compound are therefore subjects of considerable interest and possible relevance to the maintenance of iron in supersaturated solution in N_2O_4.

Possible models discussed above (Section 2(iii)) indicate that $Fe(NO_3)_3 1.5N_2O_4$ ($N_2O_3{}^+Fe(NO_3)_4^-$) or $Fe(NO_3)_3 3N_2O_4$ ($(N_2O_4)_2NO^+Fe(NO_3)_4^-$) may be recognisable entities, and either would be consistent with the observed physical and chemical properties of $Fe(NO_3)_3xN_2O_4$.

Measurement of dissociation pressures of $Fe(NO_3)_3xN_2O_4$ should elucidate the stoichiometry of stable adducts in this system.

b) Measurement of vapour pressures

Vapour pressures of N_2O_4 adducts have previously been measured in these laboratories.[28,29] However, these studies were carried out at elevated temperatures, with a view to obtaining vapour pressure vs. temperature curves and thus dissociation temperatures. It is known[30] that at about 35°C $Fe(NO_3)_3xN_2O_4$ begins partially to convert to $NO_2{}^+Fe(NO_3)_4^-$,

which may conveniently be sublimed from $Fe(NO_3)_3xN_2O_4$ at $80^oC/10^{-2}$ mm Hg, leaving a high proportion of an oxide nitrate residue.[4] Hence vapour pressure studies in the $Fe(NO_3)_3xN_2O_4$ system must necessarily be restricted to temperatures below 35^oC.

The required information in the present work is a plot of vapour pressure against x in the formulation $Fe(NO_3)_3xN_2O_4$, at a constant temperature. The investigation planned involves the study of a system of accurately known initial composition approximating to $Fe(NO_3)_3 4N_2O_4$. The vapour pressure of this system will be measured after successive removal of known amounts of N_2O_4, measured volumetrically.

An apparatus is at present under development which takes into account that long times may be necessary to attain the equilibrium vapour pressure, particularly as the composition approaches $Fe(NO_3)_3.N_2O_4$, and that pressure measurements over the range 0.1-800 mm Hg may need to be made.

(ii) Corrosion studies using a Scanning Electron Microscope

Much of the work performed so far has been based on the assumption that the N_2O_4 is saturated with iron. With the aid of a scanning electron microscope we intend to investigate the corrosion (i.e. dissolution) of iron. It is suspected that the NOCl in propellant specification N_2O_4 may be the primary corrosive agent causing the iron to dissolve.

a) General chemistry of NOCl attack on iron

As noted earlier, (Section 2(i) c)), NOCl reacts with iron to give the compound $FeCl_3.NOCl$ which undergoes solvolysis to give $Fe(NO_3)_3.N_2O_4$ and NOCl;

$$FeCl_3.NOCl + 4N_2O_4 \rightleftharpoons Fe(NO_3)_3.N_2O_4 + 4NOCl$$

Since the equilibrium in the equation lies far to the right,[4] the NOCl is regenerated and a cycle may be set up,

$$\begin{array}{ccccc} Fe & + & NOCl & \longrightarrow & [NO^+FeCl_4^-] \\ & & \nearrow & & \swarrow N_2O_4 \\ & NOCl & + & Fe(NO_3)_3.N_2O_4 & \end{array}$$

and, therefore, only a trace amount of NOCl is necessary to form (relatively) large amounts of $Fe(NO_3)_3.N_2O_4$ and thus there need be no relationship between the amount of NOCl present in the solution and the amount of corrosion finally observed. Also, the NOCl produced by solvolysis of $FeCl_3.NOCl$ will be produced at the iron surface and is immediately available for further reaction.

b) Study of metal samples

A series of solutions of NOCl in N_2O_4 will be prepared with known NOCl content (ranging from 0-600 ppm). Samples of steels will be prepared in a form suitable for examination by the scanning electron microscope, and these will be examined after immersion in $NOCl/N_2O_4$ mixtures for known lengths of time. Similar experiments could be carried out with HNO_3/N_2O_4 mixtures.

(iii) The flow apparatus

The flow apparatus is at present being modified so that N_2O_4 in the hold tank can be heated. An immersion heater is being fitted as well as a temperature controller and readout supplied by British Rototherm Ltd. While this work is in progress, the pipework and unions are being replaced with new lines of 316 stainless steel.

The test section involving a stainless steel needle valve

will continue in use but in future experiments the hold tank will be "conditioned" by heating the N_2O_4 to ca 35^oC. It may prove that "water" is not the cause of flow-decay in the N_2O_4 system. It is possible that the presence of NOCl as a contaminant may initiate corrosion. Future experiments, therefore, may include the use of N_2O_4 deliberately contaminated with small quantities of NOCl.

(iv) Mössbauer spectroscopy

This technique is applicable to a relatively small number of elements. However, ^{57}Fe happens to be the most widely investigated of all Mössbauer nuclides. The spectra of an extremely large number of iron compounds have now been recorded and the technique provides valuable information concerning the electronic environment of the Fe nucleus. In this respect it provides a valuable adjunct to other spectroscopic methods which focus attention on the lighter atoms in molecules. Mössbauer studies on dinitrogen tetroxide adducts of iron(III) nitrate and derived species will provide complementary evidence from a structural viewpoint to that furnished by e.g. vibrational spectroscopy. A Mössbauer Spectroscopy service is now available to us and advantage will be taken of it whenever appropriate during the second year of the contract.

(v) ^{14}N n.m.r. spectroscopy

The Nottingham laboratories are almost unique in the U.K. in possessing equipment for recording the ^{14}N nuclear magnetic resonance spectra of nitrogen compounds. Many diamagnetic covalent nitrato-species, including some dinitrogen tetroxide adducts e.g. $Au(NO_3)_3.N_2O_4$ $(NO^+Au(NO_3)_4^-)$ have already been

studied in these laboratories by this technique and a compilation of ^{14}N n.m.r. information on such molecules is already available. Likewise, the ^{14}N spectra of oxy-nitrogen species, e.g. NO^+, N_2O_4, N_2O_5, NO_3^-, NO_2^- etc. are now well known. ^{14}N spectra of Fe(III) nitrato-species are expected to be complicated by the effects of Fe(III) paramagnetism and a preliminary measurement on a solution of $Fe(NO_3)_3.N_2O_4$ in HNO_3 shows only one extremely broad resonance to high field of the normal covalent nitrate position and is thus relatively uninformative. Nevertheless, further ^{14}N studies (possibly over a range of temperature) of this and related iron nitrato-systems will be undertaken in order to exploit the capability of the technique for providing information on the nature of species in solution.

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